PB82-102351

Fuel NOx Control by Catalytic Combustion

Acurex Corp.
Mountain View, CA

Prepared for

Industrial Environmental Research Lab.
Research Triangle Park, NC

Sep 81

U.S. Department of Commerce
National Technical Information Service
NTIS

BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD: BEGIN SECTIONS HERE
6-1/2"
9-1/8"
BEGIN LAST LINE OF TEXT
3/8"
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
EPA-267 (Cin.) (4-76)

EPA-600/7-81-151

PB82-102351

FUEL NO_X CONTROL BY CATALYTIC COMBUSTION

by

E.K. Chu, K.D. Seifert, R.M. Kendall, and
J.P. Kesselring

Acurex Corporation
485 Clyde Avenue
Mountain View, California 94042

Contract No. 68-02-2611, Task 30

EPA Project Officer: G. Blair Martin

Industrial Environmental Research Laboratory
Office of Environmental Engineering and Technology
Research Triangle Park, North Carolina 27711

Prepared for

U.S. Environmental Protection Agency
Office of Research and Development
Washington, D.C. 20460

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA 22161

NOTICE

THIS DOCUMENT HAS BEEN REPRODUCED FROM THE BEST COPY FURNISHED US BY THE SPONSORING AGENCY. ALTHOUGH IT IS RECOGNIZED THAT CERTAIN PORTIONS ARE ILLEGIBLE, IT IS BEING RELEASED IN THE INTEREST OF MAKING AVAILABLE AS MUCH INFORMATION AS POSSIBLE.

IERL-RTP-1247	TECHNICAL REPORT DATA *(Please read Instructions on the reverse before completing)*	
1. REPORT NO. EPA-600/7-81-151	2. ORD Report	3. RECIPIENT'S ACCESSION NO. PB82 102351
4. TITLE AND SUBTITLE **Fuel NOx Control by Catalytic Combustion**		5. REPORT DATE September 1981
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) **E. K. Chu, K. D. Seifert, R. M. Kendall, and J. P. Kesselring**		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS **Acurex Corporation Energy and Environment Division 485 Clyde Avenue Mountain View, California 94042**		10. PROGRAM ELEMENT NO. 11. CONTRACT/GRANT NO. 68-02-2611, Task 30
12. SPONSORING AGENCY NAME AND ADDRESS **EPA, Office of Research and Development Industrial Environmental Research Laboratory Research Triangle Park, NC 27711**		13. TYPE OF REPORT AND PERIOD COVERED Task Final; 10/78-4/79 14. SPONSORING AGENCY CODE EPA/600/13
15. SUPPLEMENTARY NOTES **IERL-RTP project officer is G. Blair Martin, Mail Drop 62, 919/541-7504.**		

16. ABSTRACT

The report gives results of an experimental study to: (1) define operating conditions for catalytic combustors that give low levels of NOx emissions for fuel-bound nitrogen compounds, and (2) quantitatively determine the fate of fuel nitrogen during catalytic combustion. Tests were conducted with platinum and nickel oxide catalysts over a range of test conditions, using ammonia and methylamine as model fuel nitrogen compounds. Fuel NOx emissions were found to be strongly dependent on catalyst type; however, varying mass throughput, bed temperature, fuel, and fuel nitrogen type had virtually no effect on fuel NOx. The dominant nitrogenous products resulting from the catalytic combustion of a nitrogen-containing fuel were NO, N2, NH3, and HCN.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution Nitrogen Oxides Combustion Catalysis Platinum Nickel Oxides Ammonia Methylamine	Pollution Control Stationary Sources Fuel Nitrogen	13B 07B 07C 21B 07D

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21.
Release to Public	Unclassified	
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

EPA Form 2220-1 (9-73)

DISCLAIMER

This report has been reviewed by the Industrial Environmental Research Laboratory (RTP), U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

ABSTRACT

This report describes the results of an experimental study to define operating conditions for catalytic combustors that give low levels of NO_x emissions for fuel-bound nitrogen compounds, and to quantitatively determine the fate of fuel nitrogen during catalytic combustion. Tests were conducted with platinum and nickel oxide catalysts over a range of test conditions, using ammonia and methylamine as model fuel nitrogen compounds. Fuel NO_x emissions were found to be strongly dependent on catalyst type, but varying mass throughput, bed temperature, fuel, and fuel nitrogen type had virtually no effect on fuel NO_x. The dominant nitrogenous products resulting from the catalytic combustion of a nitrogen-containing fuel were NO, N_2, NH_3, and HCN.

ACKNOWLEDGEMENTS

This report presents the results of a research program to determine the conversion of fuel-bound nitrogen to NO_x or NO_x precursors under varying conditions in three different catalytic combustors. The authors wish to extend their appreciation to Dr. G. R. Lester of UOP, Inc., and W. A. Boyer of Corning Glass Works for their support in providing test materials. The contributions of H. L. Atkins, S. Hagaman, D. Knirck, T. Taylor, and J. Yoder in the preparation and testing of materials are gratefully acknowledged.

This program was conducted for the Combustion Research Branch of the Industrial Environmental Research Laboratory, U.S. Environmental Protection Agency. The EPA Project Officer was G. B. Martin, and J. A. McSorley was the Program Manager.

CONTENTS

Abstract iii
Acknowledgements iv
Figures vi
Tables vii

1. Introduction 1
2. Program Objectives and Experimental Apparatus 7
   2.1 Program objectives 7
   2.2 Experimental apparatus 8
3. Catalyst Selection 22
4. Fuel and Model Bound Nitrogen Compound Selection 26
5. Experimental Results and Discussion 28
   5.1 Screening test results 30
   5.2 Detailed test results 50
6. Conclusions and Recommendations 53
   6.1 Conclusions 53
   6. Recommendations 54

References 56

Appendices

A -- Summary of Screening and Detailed Test Data 58
B -- The Conversion of Chemically Bound Nitrogen to NO_x, NH_3 and HCN. 63
C --N_2 Concentration Measurements 75

FIGURES

Number		Page
1-1	Postulate of the initiation of homogeneous combustion by a catalytic surface	3
1-2	NO_x formation on a catalytic surface	5
2-1	Experimental apparatus	9
2-2	In-depth thermocouple placement diagram	12
2-3	Combustor mounted in test facility.	13
2-4	Prediction of nitrogenous species formation (XN = HCN + NH_3 + NO_x) based on finite reaction rates calculation	14
3-1	NH_3 conversion characteristics of natural gas doped with ammonia on NiO/Pt catalyst at 1589K (2400°F) bed temperature	25
5-1	Effect of bed temperature on NH_3 conversion to NO_x, UOP-1 catalyst	31
5-2	Effect of bed temperature on NH_3 conversion to NH_3 + HCN + NO_x UOP-1 catalyst	32
5-3	CO concentration versus theoretical air, UOP-1 catalyst	34
5-4	Effect of CO on NH_3 conversion to NO_x, UOP-1 catalyst	36
5-5	Effect of temperature on NH_3 conversion to XN, Acurex Pt catalyst	37
5-6	CO and UHC emissions versus theoretical air, Acurex Pt catalyst	39
5-7	Effects of fuel throughput on NH_3 conversion to XN at 1478K, UOP catalysts	40
5-8	Effects of fuel throughput on NH_3 conversion to XN at 1589K, NiO/Pt catalyst	42

FIGURES (CONCLUDED)

Number		Page
5-9	Effects of fuel type on NH_3 conversion to XN, UOP-1 catalyst	43
5-10	Effects of fuel type on NO conversion to NO + HCN + NH_3 in gas phase reactions, temperature = 1423K, τ_{rea} = 189 msec	44
5-11	Effects of catalyst type on NH_3 conversion to XN, Acurex Pt catalyst and NiO/Pt catalyst	46
5-12	Effect of nitrogen content on NO_x emissions, UOP-2 catalyst.	47
5-13	Effect of dopant type on NO_x emissions, UOP-2 catalyst	49

TABLES

Number		Page
2-1	Catalyst Geometric Configurations	10
2-2	Analytical Equipment Used	16
2-3	Quantitative Wet Chemistry Method	17
2-4	Gas Chromatograph Information	18
3-1	Catalyst Composition	23
5-1	Screening Test Matrix	29
5-2	Fuel-N Mass Balance	52

SECTION 1
INTRODUCTION

The current energy situation has imposed restrictions on the availability of natural gas and distillate oils for use in stationary combustion systems. The trend is to use heavier fuels, such as coal, residual oil, and synthetic fuels rather than natural gas and distillate oil. Unlike the "clean" fuels, these heavy fuels generally contain significant amounts of chemically bound nitrogen. In addition to the thermal NO_x formed during combustion through fixation of atmospheric nitrogen, this bound nitrogen can also be converted to NO_x during combustion and is generally referred to as fuel NO_x. As more stationary combustion systems switch to heavy fuels, fuel NO_x emissions will have a greater impact on the environment.

An emerging technology which shows promise in controlling both thermal and fuel NO_x emissions is catalytic combustion. As reported in Reference 1, catalytic combustors have been tested at temperatures to 2000K (3140°F) with thermal NO_x emissions less than 90 ppm corrected to 0 percent excess air. Fuel NO_x control through the use of a two-stage catalytic combustion system is also reported in Reference 1, with NH_3-doped natural gas used to simulate a nitrogen-containing fuel. Conversions of bound nitrogen to NO_x and precursors (HCN and NH_3) as low as 11 percent were measured for this system.

A catalytic combustion system is a hybrid system having some of the combustion characteristics of premixed and diffusional flames. The catalytic combustor uses premixed fuel and air, and the combustion process is controlled by the diffusion of reactants to the reaction zone located at the surface of the catalyst. Since the diffusional process in a monolith cell is inversely dependent on the cell diameter, i.e.,:

$$Sh = \frac{hd}{D}$$

where Sh is the Sherwood number, h is the mass transfer coefficient, d is the cell diameter, and $\mathcal{D}$ is the diffusivity, the combustion process in catalytic reactors can thus be controlled by the reactor geometry. For example, a catalytic reactor with large cell size will require a longer reactor bed than a catalytic reactor with small cell size for complete combustion. Thus, unlike premixed flames in which the combustion process occurs within milliseconds, the residence time for catalytic combustion can be either prolonged by using large cell size monoliths or reduced by using small cell size monoliths. With this additional dimension of control, other reactions of special interest, such as nitrogenous species reactions, may be controlled concurrently with the combustion process. By proper system optimization, there is a potential that fuel NO_x formation can be controlled by a catalytic combustion system.

A schematic diagram depicting the combustion phenomena occurring in one cell of a monolithic catalytic combustor is shown in Figure 1-1. At the front of the combustor, the combustion zone is sustained at the catalytic surface by the diffusion of the reactive mixture from the bulk gas across the boundary layer. The heat generated as a result of surface combustion will then be fed back to the bulk gas stream by convective and radiative heat transfer and diffusion of the combustion products. As the bulk gas mixture becomes hotter and the boundary layer grows thicker, the flame speed is correspondingly increased and the flow velocity lowered near the surface. The combustion zone then starts to propagate across the boundary layer wherever the flame speed is greater than the flow velocity. Finally, the bulk gas mixture ignites when the following conditions are reached:

$$\left.\frac{\partial u}{\partial y}\right|_{wall} < \frac{S}{\delta} \tag{1}$$

and

$$u_{bulk} = S \tag{2}$$

where $\partial u/\partial y|_{wall}$ is the velocity gradient at the wall, S is the flame speed, δ is the quenching diameter, and u_{bulk} is the bulk gas velocity. Equations

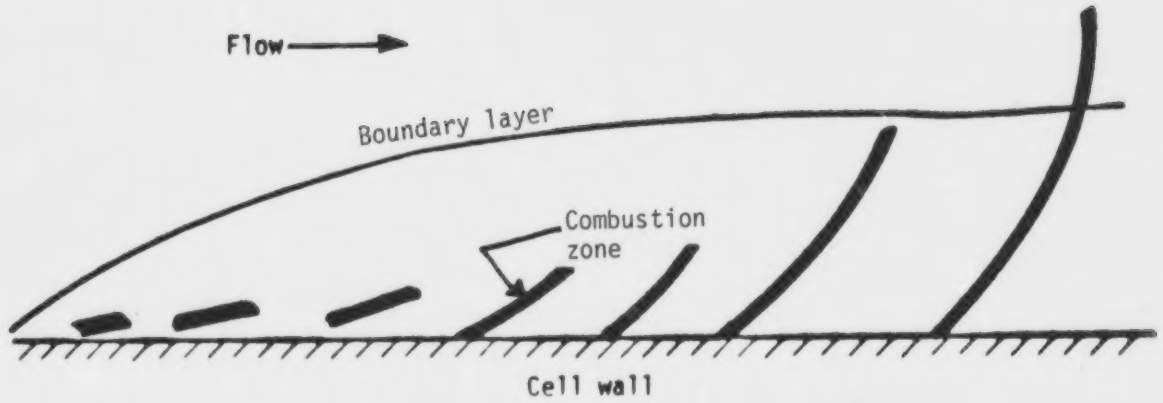


Figure 1-1. Postulate of the initiation of homogeneous combustion by a catalytic surface.

(1) and (2) also show that suppression of homogeneous combustion could be achieved by either increasing the mass throughput or by decreasing the bed temperature. Increases in mass throughput increase the velocity gradient at the wall and the flow velocity, and therefore inhibit homogeneous combustion. Decreases in bed temperature lower the gas temperature and indirectly the flame speed, and therefore also inhibit homogeneous combustion.

For the conversion of chemically bound nitrogen in a catalytic combustion system, the phenomena depicted in Figure 1-2 are assumed and these phenomena are described as follows:

- Premixed fuel and air are introduced into the combustor, and diffuse to the catalytic surface across the developing boundary layer
- Pyrolysis of the fuel and chemically bound nitrogen to intermediate species occurs in the boundary layer
- Conversion of chemically bound nitrogen to NO_x or N_2 at the catalytic surface when reacting with oxygen or other oxidation species
- Reaction of NO_x with reduction species such as CH, CO, and NH_i to form N_2 inside the boundary layer as NO_x diffuses back to the free stream

The subject of fuel nitrogen conversion in catalytic combustion systems has been examined by Matthews and Sawyer (Reference 2). Trace amounts of either nitric oxide or ammonia were added to propane/oxygen/argon mixtures and combusted on a platinum catalyst under rich, stoichiometric, and lean combustion conditions. Conversion of the two model fuel nitrogen compounds to nitric oxide was measured as a function of equivalence ratio, adiabatic flame temperature, and fuel nitrogen concentration. Since the monolithic catalyst bed was uninsulated during operation, the measured bed temperatures were much lower than the corresponding adiabatic flame temperatures. For this operational mode, the conversion of fuel nitrogen to NO_x was found to be strongly dependent on equivalence ratio, weakly dependent on calculated adiabatic flame temperature, and moderately dependent on fuel nitrogen concentration. The precise fate of the fuel nitrogen was not determined.

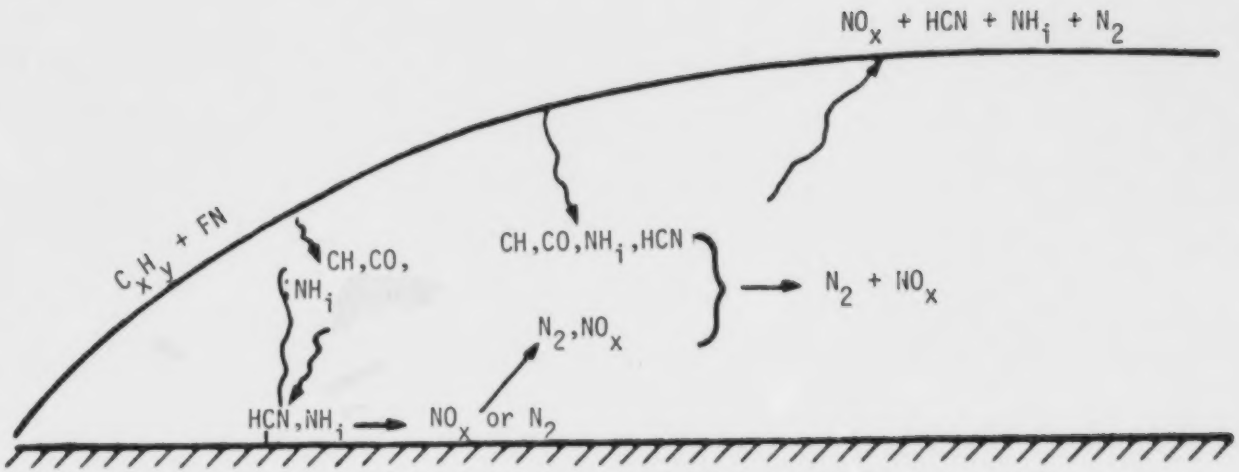


Figure 1-2. NO_x formation on a catalytic surface.

The fate of fuel nitrogen in backmixed combustion has been determined by Corlett and Monteith (Reference 3). Nitrogenous additives such as pyridine, nitric oxide, and ammonia were added to a propane/oxidant stream and burned in a jet-stirred reactor. Tests with air as the oxidant suggested that the dominant nitrogenous species were nitric oxide, ammonia, hydrogen cyanide, and molecular nitrogen. Tests using argon/oxygen to replace the atmospheric air were conducted to establish a nitrogen balance. On the basis of the four species mentioned above, a balance within 10 percent was generally established.

The study reported here was conducted to achieve two objectives. First, the study was to define operating conditions for catalytic combustors giving low levels of NO_x emissions. Second, the study was to conduct a systematic experimental determination of the fate of fuel nitrogen during catalytic combustion. The remainder of this report gives the results of the study.

SECTION 2
PROGRAM OBJECTIVES AND EXPERIMENTAL APPARATUS

In this section, a detailed statement of the program objectives is given and the experimental apparatus is described.

2.1 PROGRAM OBJECTIVES

The purpose of this study was to evaluate the parameters which affect the conversion of chemically bound nitrogen to NO_x during catalytic combustion, and to define conditions giving low levels of NO_x. Specifically, the following parameters were examined:

- Catalyst type
- Percent theoretical air
- Mass throughput
- Reaction temperature
- Fuel bound nitrogen content
- H_2S additive

An understanding of the effects of the above parameters is essential to the development of a low NO_x catalytic combustor.

The fate of chemically bound nitrogen during catalytic combustion was also determined in this study using an argon/oxygen mixture as the oxidant. The results from this part of the study provide further insight into the reaction mechanisms of the bound nitrogen conversion. A direct comparison of results for argon/oxygen testing and air testing is difficult. Since argon has a much lower specific heat but nearly the same molecular weight as nitrogen, in order to maintain the same catalyst temperature for a given fuel/oxygen ratio requires a larger volumetric flowrate of argon than of nitrogen. This difference in volumetric flowrates produces a different residence time for the two tests, and hence a direct comparison of results is not possible.

2.2 EXPERIMENTAL APPARATUS

Figure 2-1 illustrates the experimental apparatus. For simplicity, the equipment can be divided into the following five categories:

- Flow metering and measurement systems
- Preheating system
- Combustor and housing
- Probe and sample transfer system
- Analytical equipment

Each of the above categories will be individually discussed in the following subsections.

2.2.1 Flow Metering and Measurement Systems

As illustrated in Figure 2-1, the following components of the reactive mixtures can be metered in the system:

- C_3H_8/CH_4/natural gas
- Air/argon
- N_2/O_2
- NH_3/CH_3NH_2
- H_2S

The first three sets of components were metered at both low and high flowrates through the use of pairs of rotameters, one covering the high range and the other the low range. A tri-flat variable area low flow rotameter, manufactured by Fischer and Porter Co., was used to meter the ammonia and methylamine flowrates. This rotameter was specifically calibrated for ammonia by Homer-Dulin Co. in Long Beach, California in order to achieve the high degree of accuracy needed in monitoring the amount of nitrogen species feeding into the system. The meter accuracy was checked by comparison with wet chemistry measurements of unreacted ammonia, and satisfactory agreement was obtained.

2.2.2 Preheating System

As illustrated in Figure 2-1, only the oxidant is allowed to pass through the main heater, which consists of a series of six 6000 watt exposed-element heaters (GTE Sylvania Model 138825, Style A). The preheat temperature is electronically controlled by use of a proportional controller (Chromalox series C76, O-811K) in conjunction with a silicon controlled

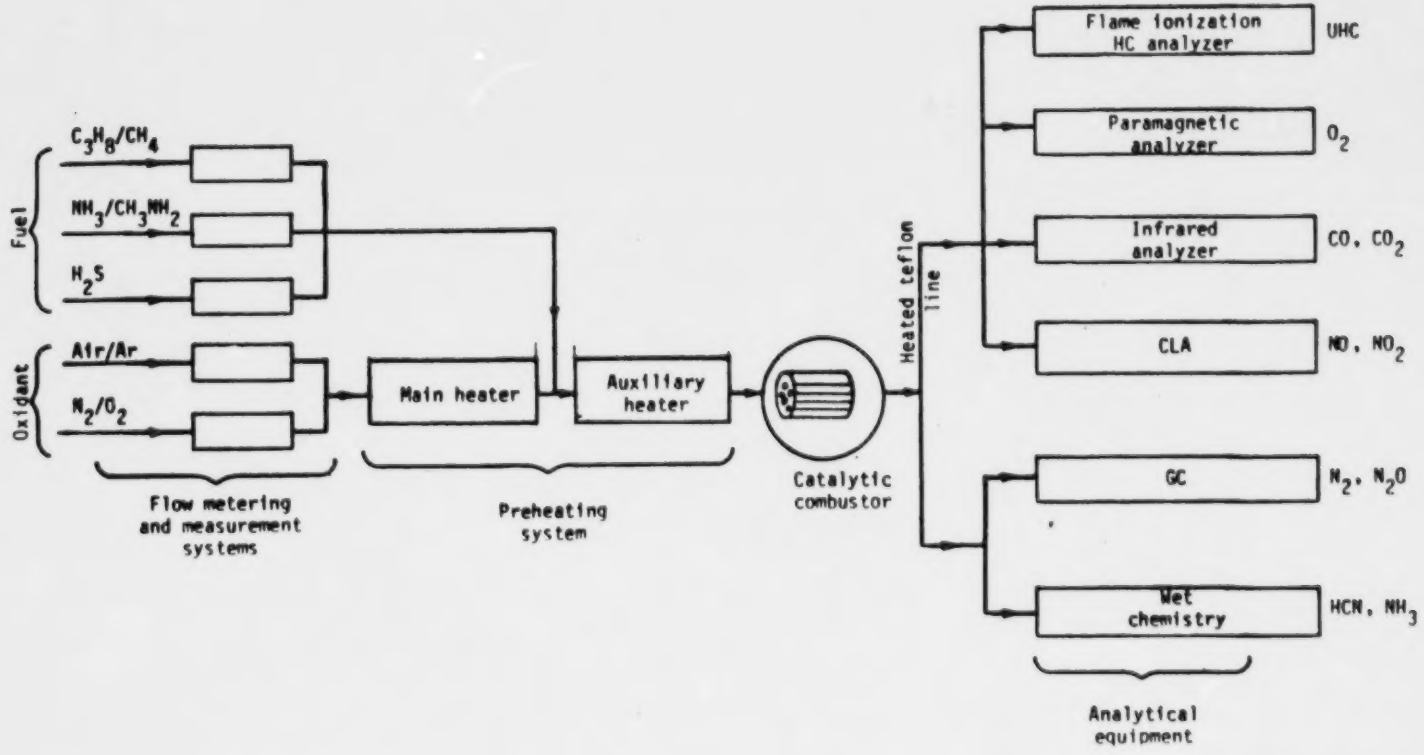


Figure 2-1. Experimental apparatus.

rectifier (Chromalox Thyristor Power Controller Model CSCR 005-1208-60) effectively pulsing the current to the heaters in 1/60 second increments every 1/3 second.

The fuel, however, bypasses the main heater to avoid preignition hazards within the main heater, and passes through a flame arrester before mixing with the oxidant. This fuel/oxidant mixture then passes through the mixing chamber and flow straightener before arriving at the catalytic combustor. During this time, the preheat temperature of the gas mixture is maintained by an auxiliary heater (Thermocraft, 3400 watt) jacketed around the exterior of the mixing chamber.

2.2.3 Combustor and Housing

A 0.0457 m (1.8 inch) I.D. fused quartz tube was used to house the combustor. The combustor was mounted inside the quartz tube by inserting a thin-walled inner quartz tube to support the combustor's weight and by wrapping a thin layer of fiberfrax around the combustor to provide firm contact with the inner surface of the outer quartz tube.

The combustor consisted of three 0.025 m (1 inch) segments of graded cell catalyst. Table 2-1 lists the four different catalysts tested and

TABLE 2-1. CATALYST GEOMETRIC CONFIGURATIONS

Catalyst Type	Large Cell Diam, m (in)	Intermediate Cell Diam, m (in)	Small Cell Diam, m (in)
UOP-1	6.35×10^{-3} (0.25)	4.76×10^{-3} (0.1875)	1.59×10^{-3} (0.0625)
UOP-2	4.76×10^{-3} (0.1875)	4.76×10^{-3} (0.1875)	1.59×10^{-3} (0.0625)
Acurex Pt/NiO	6.35×10^{-3} (0.25)	4.76×10^{-3} (0.1875)	1.59×10^{-3} (0.0625)
Acurex Pt	6.35×10^{-3} (0.25)	4.76×10^{-3} (0.1875)	1.59×10^{-3} (0.0625)

gives information on the cell sizes used. Two UOP catalysts were required when it became impossible to sustain stable combustion on UOP-1 after several hours of testing. As noted in Table 2-1, UOP-2 used only intermediate and small cells due to the long lead time required to obtain additional large cell segments from UOP. Nearly identical performance was obtained from the two UOP catalysts. Further information on catalyst selection is given in Section 3.

Five K-type thermocouples were placed in the beds to monitor in-depth combustion temperatures. The locations of these thermocouples are shown in Figure 2-2. In addition to these five thermocouples, a thermocouple located at the combustor exit monitored the exhaust gas temperature.

Outside of the quartz tube housing, a thickness of approximately 6 inches of insulation was applied to minimize heat losses from the combustor. A window was cut through the insulation to give a physical view of the reactor during combustion. Figure 2-3 shows the combustor and housing as mounted in the test facility.

2.2.4 Probe and Sample Transfer System

A water-cooled stainless steel sample probe was used in this experiment. This probe was selected because of its durability in a hostile environment. The probe is capable of reducing NO_2 to NO catalytically unless the sample has been sufficiently quenched. Hence, the actual measurement of NO and NO_2 may not be completely reliable. Nevertheless, from studies of homogeneous combustion (Reference 4), NO_2 exists only in the flame zone. In the near post-flame region the concentration of NO_2 is generally low as a result of rapid conversion from NO_2 to NO. If the same analogy were drawn, NO_2 concentration should also be low in this study.

Under fuel-rich conditions, it is possible for residual reactions to occur inside the sampling probe, leading to the reduction of NO_x to other nitrogenous species. To minimize the effect of reactions inside the probe, the sample gas is required to be quenched at a rate of 10^6 K/sec or higher. This requirement is necessary for the design of probes used to sample chemical species in the pre-flame and flame zones where an extremely nonequilbrium thermodynamic state is encountered. In the post-flame zone, however, the nitrogenous species asymptotically approach a steady state value (see Figure 2-4); and hence such a stringent requirement may not be necessary. In

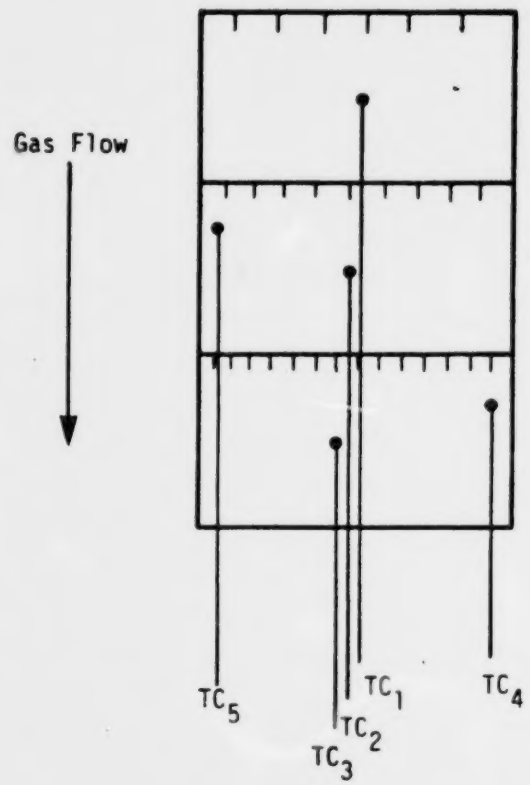


Figure 2-2. In-depth thermocouple placement diagram.

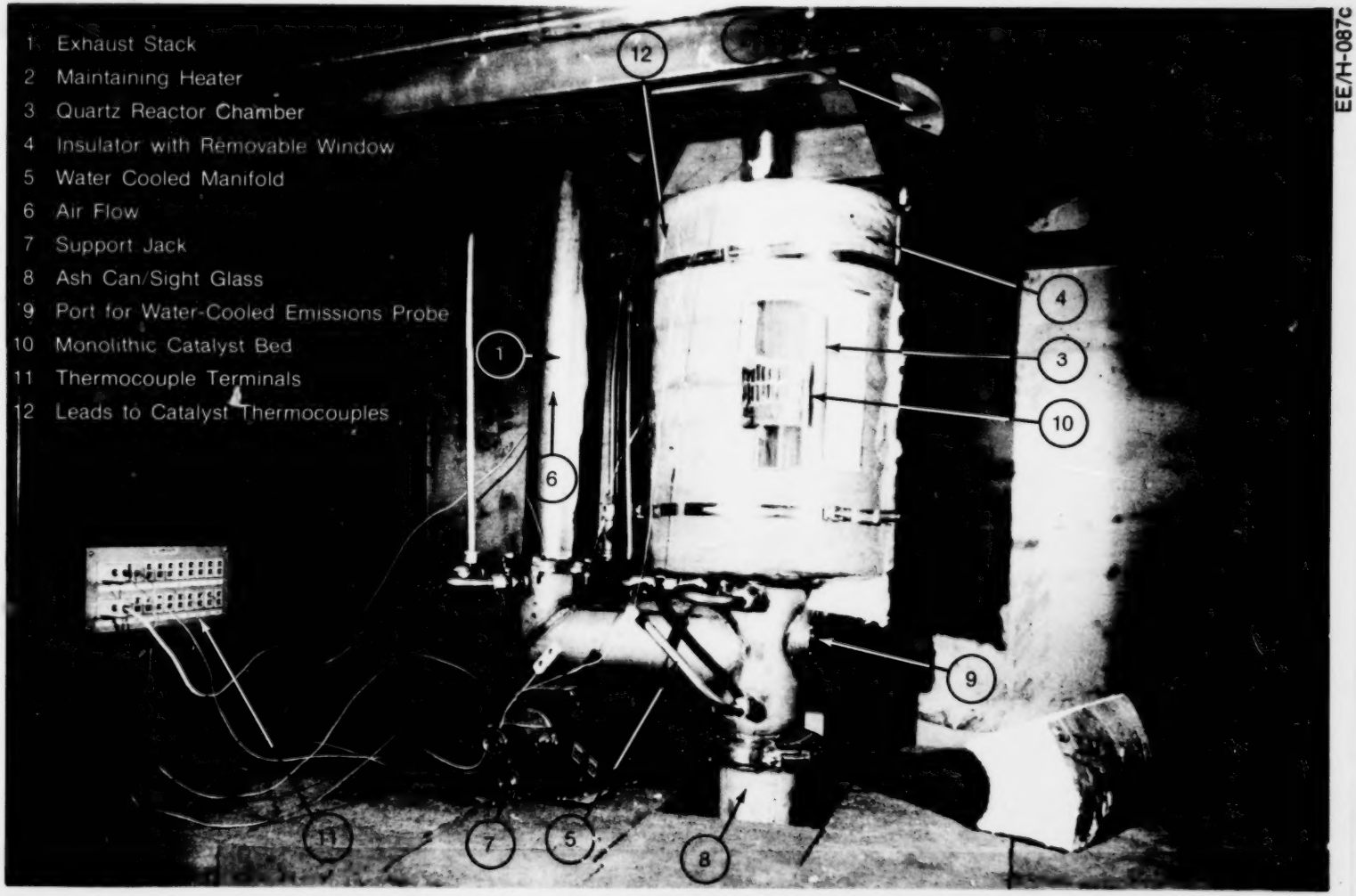


Figure 2-3. Combustor mounted in test facility.

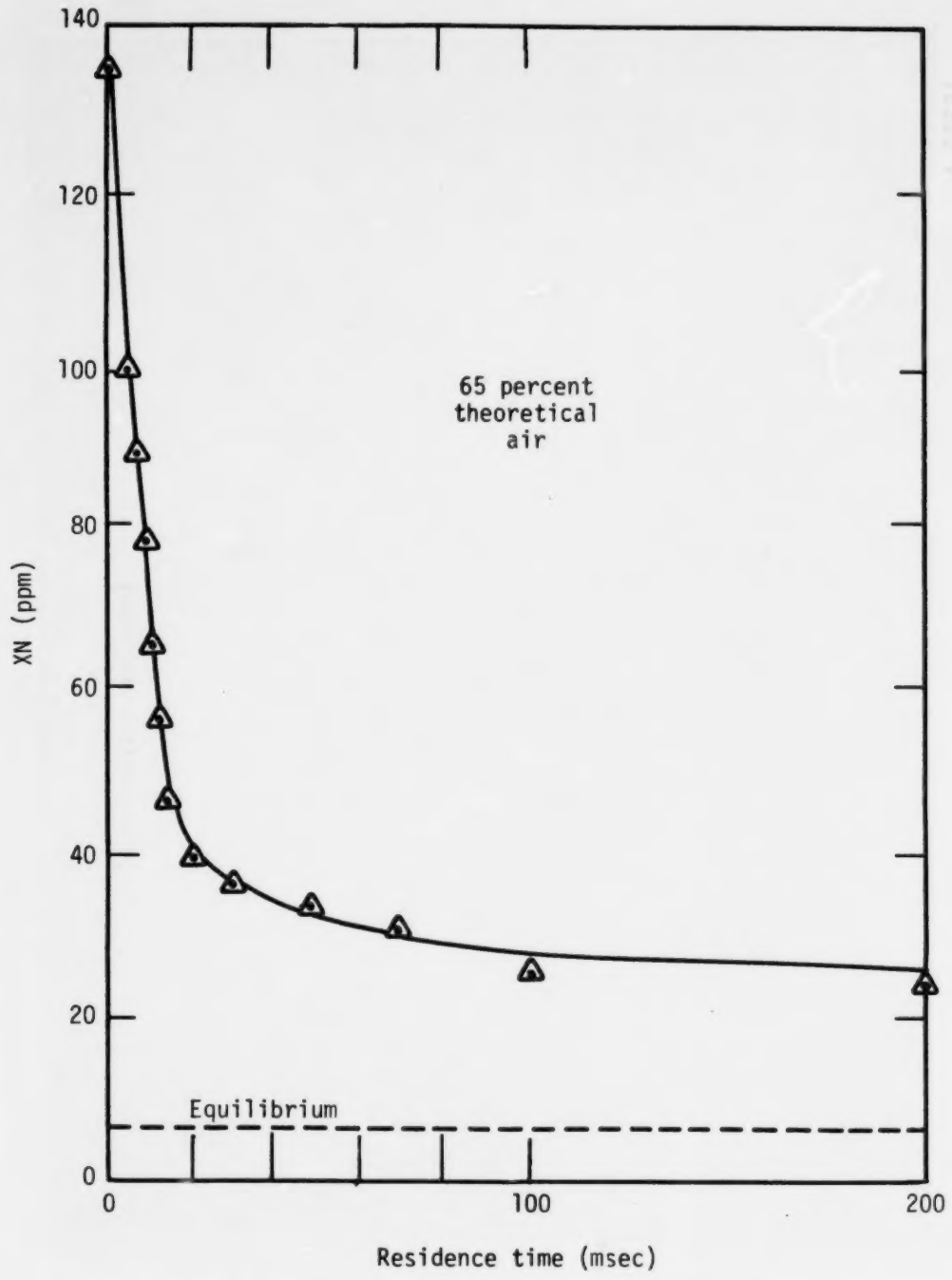


Figure 2-4. Prediction of nitrogenous species formation ($XN = HCN + NH_3 + NO_x$) based on finite reaction rates calculation (Reference 5).

addition, the probe surface temperature was designed to be maintained at a temperature below 350K, and thus possible catalytic reactions prompted by the stainless steel surface were minimized. The more sophisticated micro water-cooled quartz probe was not used in this experiment since it has been observed that both NH_3 and HCN can sorb irreversibly on hot quartz surfaces (Reference 6).

The sampling probe was located 0.10 m (4 inches) downstream of the catalytic combustor. This short distance was used to minimize any potential system contamination of the combustion products. The hot exhaust gas was then quenched at a rate of 1.2×10^5 K/sec to about 339K (150°F) to prevent further reactions from occurring in the gas phase.

Part of the exhaust was drawn directly either to the wet chemical analysis setup or to the gas chromatograph, both of which were located next to the housing of the combustor. The short distance from the sampling probe to this equipment should minimize the possibility of loss of HCN and NH_3 species to condensation occurring in the sample transfer system.

The other part of the exhaust gas was transferred in a 9.5×10^{-3} m (0.375 inch) O.D. heated teflon line to the emission bench, where CO, CO_2, UHC, O_2, and NO_x were measured. The temperature of the sample line was maintained at approximately 339K (150°F) at all times to prevent water condensation within the sample transfer system.

2.2.5 Analytical Equipment

Table 2-2 summarizes the analytical equipment used and the corresponding chemical species measured. Since the emphasis of this study was on the measurement of the nitrogen species, only the corresponding equipment will be discussed in this section. This equipment includes:

- Wet chemical analysis
- Gas chromatograph
- Chemiluminescent analyzer

2.2.5.1 Wet Chemical Analysis

The wet chemistry setup consisted of a series of four Pyrex glass impinger bottles with the necessary Pyrex connectors immersed in an ice water bath. The first impinger bottle contained 0.005 N H_2SO_4 which preferentially dissolved NH_3. The second bottle contained 0.2 N NaOH which preferentially dissolved HCN. The third bottle contained deionized water, and was

TABLE 2-2. ANALYTICAL EQUIPMENT USED

Chemical Species	Method	Detection Range	Equipment Model
NH_3	Absorbed in 0.005 N H_2SO_4		Orion 951000
	Ammonia -- Sensing Electrode	2-10 ppm	
	Direct Nesslerization (Colorimetric)	>10 ppm	
HCN	Absorbed in 0.2 N NaOH		Chemtrix Cn1015 M
	Cyanide Ion-Selective Electrode	<10 ppm	
	Titrimetric -- Silver Nitrate Solution	>10 ppm	
N_2	G.C: Silica Gel & Molecular Sieve 5A Columns	>50 ppm	Carle G.C. 8700
N_2O	G.C: Poropac Q Column	>50 ppm	Carle G.C. 8700
CO	Infrared Absorption	0-2000 ppm	Hartman & Braun Uras 2T/CO
CO_2	Infrared Absorption	0-20%	Hartman & Braun Uras 2T/CO_2
O_2	Paramagnetic Detection	0-21%	Hartman & Braun Magnos 5T
UHC	Flame Ionization	0-100,000 ppm	Beckman Model 400 HC Analyzer
NO, NO_x	Chemiluminescent Analyzer	0-10,000 ppm	Air Monitoring Inc. Model 32 C (Atmospheric)

used to dissolve the remaining NH_3 and HCN in the sample gas which might be carried past the first two bottles. The fourth bottle contained a drying agent which dessicated the gases before passing to a gas volume meter, pump, and flowmeter, to prevent damage to these instruments.

After placing fresh solutions in the first three impinger bottles, the entire system was leak checked by evacuating the air space in the bottles. If an air leak was present, all junctions were regreased with vacuum grease. This procedure was repeated until no air leak was observed. Then, a known volume of sample gas was drawn through the impinger set at an optimal sampling rate. Finally, the individual solutions were analyzed by quantitative methods as summarized in Table 2-3 to determine the NH_3 and HCN concentrations.

TABLE 2-3. QUANTITATIVE WET CHEMISTRY METHOD

	NH_3	HCN
Absorbent	0.005 N H_2SO_4	0.2 N NaOH
Quantitative Method	• Ammonia-sensing electrode, conc. <10 ppm, Detection limit 2 ppm • Direct nesslerization method, conc. >10 ppm	• Cyanide-ion-selective electrode, conc. <10 ppm • Titrimetric method -- silver nitrate solu., conc. >10 ppm
Max error	2%	2%

2.2.5.2 Gas Chromatograph

The gas chromatograph was used specifically to measure nitrogen and nitrous oxide concentrations in the exhaust gas when argon/oxygen was used as the oxidant. A characterization of the gas chromatograph and operational procedure is presented in Table 2-4.

TABLE 2-4. GAS CHROMATOGRAPH INFORMATION

	Nitrogen	Nitrous Oxide
Instrument	Carle G.C. 8700	Same
Detector	Thermal Conductivity Equipment with a 8-10K, 0.013 in diam. Thermistor	Same
Detector Temperature	200°C	Same
Column Temperature	23°C	23°C
Flowrate (He)	20 ml/min	20 ml/min
Sample Size	1 ml	1 ml
Column	1A: 8 ft x 1/8 in. Silica Gel 1B: 6 ft x 1/8 in. Molecular Sieve 5A	1: 6 ft x 1/8 in. Poropac Q
Retention Time	4:25 min	4:00 min
Detection Limit	50 ppm	50 ppm
Program	• Purge sample loop for 5 min. • Sample for 10 sec • 39 sec after injection switch from series to bypass • 2 min switch back to series and complete run	• Purge syringe • Store sample gas in syringe • Inject 1 ml sample in G.C.

2.2.5.3 Chemiluminescent Analyzer

The Intertech model 32C chemiluminescent analyzer (CLA) was used for NO measurement. Built into this analyzer is a bypassable heated stainless steel catalytic converter intended to reduce NO_2 to NO, thus providing an additional option of measuring NO_x. This feature, however, is useful only for near stoichiometric to lean conditions since the presence of N compounds (NH_3 and HCN), CO, and UHC can substantially affect the converter's performance and therefore the NO_x measurement. To circumvent the interference from these species, a molybdenum catalytic converter should be used. Since this capability is not available on the Acurex equipment, NO_x measurements were not made under fuel-rich conditions.

Concerns have been expressed regarding the accuracy of using a chemiluminescent analyzer for measuring NO concentrations. Matthews and Sawyer (Reference 2) have shown that one of the factors which may affect NO measurements when using the chemiluminescent analyzer is the dependence of the chemiluminescent intensity on competing third body quenching reactions. Since chemiluminescent analyzers are usually calibrated with a mixture of NO in N_2, the indicated measurement of NO can be affected if the composition of the sample gas is different from the calibration gas because of a difference in third bodies. Two of the more difficult species are H_2O and argon, with H_2O being an efficient quenching agent and argon being a poor quenching agent.

D. J. Seery of UTRC (Reference 7) investigated a chemiluminescent analyzer calibrated by the usual NO/N_2 mixture, with a sample gas mixture of NO/argon supplied by Matheson Gas Products Company. The CLA measurement was then compared with both the mass spectrometer measurement using the same sample gas and the sample gas specifications supplied by Matheson. The CLA measurement was similar to that of the gas supplier but was lower than the mass spectrometer measurement. After a thorough investigation he concluded that the mass spectrometer measurement was the more correct result. This finding seems contradictory to that of Matthews and Sawyer. However, Seery indicated that his experiment with the chemiluminescent analyzer was in an operating regime where the difference in third bodies was not the dominant factor. His CLA has been modified such that the mixture ratio

between the ozonated oxygen and the sample gas in the reaction chamber is 10 to 1. Hence, the adverse third body quenching effect introduced by H_2O and Ar can be minimized. Seery concluded that his results could be attributed to the difference in viscosity for the calibrated gas and the sample gas. Since the viscosity affects the flowrate, the mixture ratios in the reaction chamber for both cases were therefore different, thus affecting the NO measurement.

D. Pershing and Rocketdyne have both investigated their chemiluminescent analyzers. Both concluded that no significant effect was observed. According to Pershing (Reference 8), the viscosity effect and the third body quenching effect may have counterbalanced each other, and therefore no significant effect was observed.

A detailed study which specifically addressed these uncertainties has been performed by B. A. Folsom and C. W. Courtney of EER Corporation (Reference 15). Two commercially available CLAs, including a Beckman Model 951 and a TECO Model 10A, were tested to study their sensitivity to NO in different carrier gases prepared to simulate various combustion products. The simulated combustion products were prepared by using a flow metering system with accuracy better than 5 percent for each component gas and were doped with known quantities of NO. By using a systematic approach, the effects of each component gas of the simulated gas mixture on the CLAs' sensitivity to NO were then determined. The conclusions of their study are summarized as follows:

1. The errors introduced by neglecting sample background gas composition variations cover the following ranges:

Combustion Products from fuel and:	Error % TECO	Beckman
21% O_2/N_2	+1 to -5	+2 to -11
21% O_2/Ar	-11 to -16	-6 to -14
21% O_2/21% CO_2/Ar	-12 to -15	-15 to -20

2. CO_2, H_2O, O_2, and Ar (if Ar/O_2 mixtures are used instead of air are the major constituents in the combustion products that decrease the CLAs' sensitivity to NO. At near stoichiometric conditions,

CO_2 accounts for the majority of the errors in NO measurements. Water vapor has a much higher quenching efficiency than N_2 and thus can change the CLA response to NO by several percent by varying the sample dew point temperature. High concentrations of O_2 present in the sample, typical of lean combustion products, result in errors as high as 4 percent. The effects of viscosity and quenching variations are opposite for argon. However, the viscosity related variations appear to overcompensate for the quenching variations, resulting in a decrease in CLA sensitivty to NO with increasing Ar concentration. For experiments utilizing O_2/Ar or O_2/Ar/CO_2 as the oxidant, errors as high as 20 percent can be realized.

3. The variations in CLA response due to background gas composition variations were generally smaller with the TECO instrument than with the Beckman except for argon. For monitoring samples from fuels burned in air, a low reaction chamber pressure CLA such as the TECO would be preferred. However, the choice of instruments for experiments involving O_2/Ar or O_2/CO_2/Ar oxidants is unclear.

From the above investigators' results, the effects on CLA measurements due to the difference in composition between the sample gas and calibration gas are strongly dependent on the operating regime of the equipment. In this study, no special effort was taken to evaluate the abovementioned effects on the system. It was felt that such special effort was not required since the sample gas in the screening tests was composed largely of N_2, whereas in the detailed tests only low NO_x conditions were tested and hence extremely accurate NO measurements were not required.

SECTION 3
CATALYST SELECTION

Catalysts selected for this study included systems manufactured by Universal Oil Products Company (UOP) and Acurex Corporation. The UOP catalyst was a proprietary combustion catalyst system manufactured for research purposes. The Acurex catalysts were platinum and platinum/nickel oxide research systems. All catalysts were prepared on graded cell Torvex alumina monoliths supplied by E. I. DuPont de Nemours, Inc., and similar systems have been combustion-tested in another EPA research and development program (see Reference 1). Table 3-1 gives details on the catalyst composition data. The catalyst types selected were to give comparisons between a platinum catalyst (Acurex-1), a base metal oxide catalyst (Acurex-2), and a catalyst supplied by a major catalyst manufacturer (UOP-1 and UOP-2).

Results described in Reference 1 indicate that, for the temperature range of 1347 to 1478K, the UOP catalyst performed extremely well. While the catalytic activity of the UOP catalyst in terms of fuel conversion efficiency was comparable to that of the Acurex platinum catalyst, the UOP catalyst had exceptional lightoff capabilities, bed temperature uniformity, and sustained activity performance. The Acurex base metal oxide is a high temperature catalyst requiring a minimum reaction temperature of 1589K for stable operation.

A catalyst similar to Acurex-1, the platinum catalyst, had previously been tested for fuel nitrogen conversion. The limited testing with ammonia dopant showed that for rich combustion conditions (theoretical air between 28 and 42 percent), nearly all NH_3 dopant was emitted as NH_3. Under lean conditions, however, preliminary data reported in Reference 1 show conversions of NH_3 dopant to NO were measured at 23 percent for one-atmosphere combustion and at 70 percent for three-atmosphere combustion. Later data,

TABLE 3-1. CATALYST COMPOSITION

MANUFACTURER	CATALYST/WASHCOAT/SUPPORT	CATALYST LOADING, WT. %
UOP-1	UOP Proprietary/DuPont alumina	–
UOP-2	UOP Proprietary/DuPont alumina	–
Acurex-1	Pt/DuPont AA washcoat/DuPont alumina	6.76/4.03/6.09
Acurex-2	NiO-Pt/DuPont AA washcoat/DuPont alumina	2.51/0/0 Pt 4.74/6.11/8.44 NiO

also reported in Reference 1 and obtained on an advanced graded cell model gas turbine system with a UOP catalyst, showed conversions of NH_3 dopant to NO of 65 percent at one atmosphere, 60 percent at three atmospheres, and 41 percent at eight atmospheres. Differences between the preliminary data on the Acurex platinum catalyst and the later data for the UOP catalyst may be a result of differences in mass throughput rates or bed temperatures. Additional testing is required to completely define the effects of pressure on NH_3 conversion.

An early version of Acurex-2, the NiO/Pt catalyst, was tested extensively for fuel nitrogen conversion. As shown in Figure 3-1, the sum of NH_3, HCN, and NO species was minimized at 75 percent theoretical air. The promise shown by this catalyst for application to low NO_x two-stage combustion is apparent.

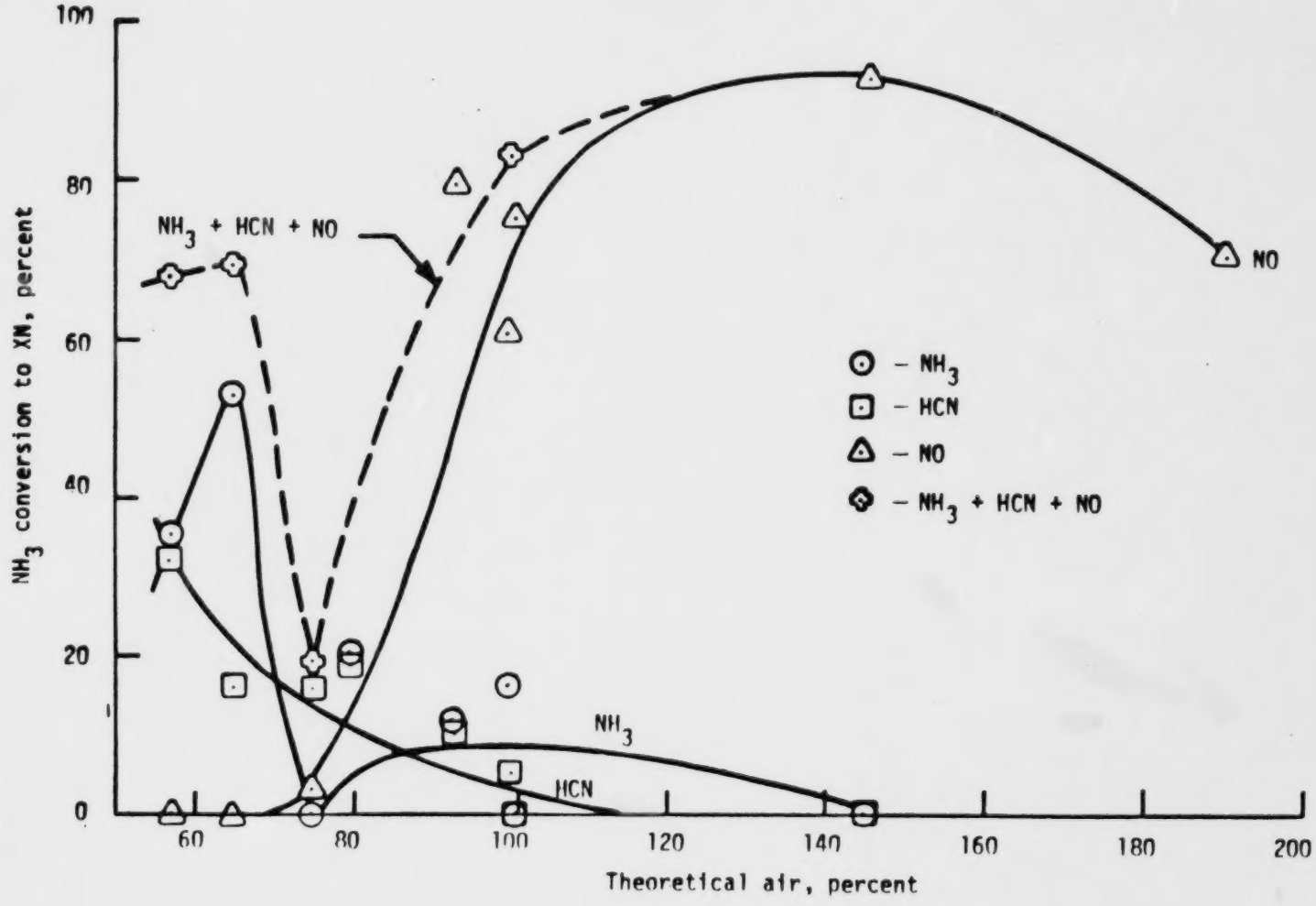


Figure 3-1. NH_3 conversion characteristics of natural gas doped with ammonia on NiO/Pt catalyst at 1589K (2400°F) bed temperature.

SECTION 4
FUEL AND MODEL BOUND NITROGEN COMPOUND SELECTION

Propane and natural gas were the fuels selected for this study. Propane was chosen as the main fuel because its combustion characteristics closely resemble those of commercial fuels, even though the oxidation kinetics are not well understood. Natural gas, on the other hand, has fairly well understood oxidation kinetics, but exhibits characteristics which are different from most other hydrocarbons. Consisting mostly of methane, natural gas has a C-H bond energy on the order of kilocalories greater than that for other hydrocarbon fuels. As a result, the oxidation reaction rate of natural gas is slower than for most other hydrocarbon fuels. This characteristic can thus be used to evaluate the effect of fuel type (due to the difference in reaction rates) on the conversion of chemically bound nitrogen to NO_x.

Homogeneous combustion studies (Reference 9) give strong evidence that the rate-controlling steps in the conversion of bound nitrogen to NO_x and N_2 are independent of the molecular structure of the bound nitrogen compound. Though it is believed that the same phenomenon should be observed in catalytic combustion, this had not been verified by experiments.

To verify the same phenomenon occurs during catalytic combustion, two model bound nitrogen compounds were used in this study; methylamine and ammonia. Since methylamine has a chemical structure which consists of a C-N bond, the following reactions are required to occur before it reaches the final pyrolysis products which are mostly NH_3 and HCN:

$$\left.\begin{aligned} CH_3NH_2 &\rightarrow HCN + 2H_2 \\ CH_3NH_2 + H_2 &\rightarrow CH_4 + NH_3 \end{aligned}\right\} \text{Thermal pyrolysis}$$

$$2CH_3NH_2 + O_2 \rightarrow 2CH_2 + 2NH_3$$
$$CH_3NH_2 + O_2 \rightarrow CO + H_2O + NH_3$$
$$CH_3NH_2 + O_2 \rightarrow HCN + 2H_2O$$
$$2CH_3NH_2 + 3O_2 \rightarrow 2CO_2 + 2H_2O + 2NH_3$$

} Oxidative pyrolysis

Although methylamine is in fact a simpler compound than that which exists for chemically bound nitrogen, results from its use serve the purpose of inferring the importance of pyrolysis in the conversion of bound nitrogen to NO_x.

SECTION 5
EXPERIMENTAL RESULTS AND DISCUSSION

Two experimental test series were performed to fulfill the program objectives: screening tests and detailed tests. Using air as the oxidant and nitrogen as the diluent, the screening tests were designed to study the effects of the following parameters on the chemically bound nitrogen conversion process:

- Percent theoretical air
- Bed temperature
- Fuel throughput
- Fuel type
- Catalyst type
- Chemically bound nitrogen type

The primary screening dependent variables measured include NO and NO_2 in fuel-lean conditions and NO, HCN, and NH_3 in fuel-rich conditions. A test matrix for the screening tests is presented in Table 5-1.

The detailed tests focused on the determination of the fate of chemically bound nitrogen during catalytic combustion in low NO_x conditions. In order to identify the portion of the fuel nitrogen converted to N_2 (the most environmentally desirable compound) and to determine closure of the nitrogen balance, an oxygen/argon mixture was used instead of an air/nitrogen mixture for oxidizer and diluent agents. Nitrogen species concentrations measured include NO, NO_2, N_2, N_2O, NH_3, and HCN, assuming that these species were the dominant products of the chemically bound nitrogen conversion process. A nitrogen mass balance was then performed to verify the above assumption. Tests performed in this series include both fuel-rich and stoichiometric conditions where NO_x emissions are low, conditions with variable chemically bound nitrogen content, and conditions with the coexistence of H_2S.

TABLE 5-1. SCREENING TEST MATRIX

	Temperature, °F Fuel Throughput, Btu/hr	UOP-1 and UOP-2			Acurex Pt	Acurex NiO/Pt
		Fuel nitrogen dopant			Fuel-N dopant	Fuel-N dopant
		Nominal NH_3 (0.3-0.5%)	Variable NH_3	Nominal CH_3NH_2	Nominal NH_3 (2%)	Nominal NH_3 (2%)
Natural gas	2200°F 24,000 Btu/hr	THF				
	2200°F 40,000 Btu/hr	CTHF				
	2000°F 24,000 Btu/hr	TH				
	2000°F 40,000 Btu/hr	TH				
Propane	2200°F 24,000 Btu/hr	HF	N			2400°F ↑ H
	2000°F 40,000 Btu/hr	HFD		D		2400°F ↓ HC
	2200°F 40,000 Btu/hr				CT	
	2000°F 40,000 Btu/hr				CT	

Symbol	Effect	Figures	Comments
T	Bed temperature	5.1-5.6	Variable rich to lean stoichiometry
H	Fuel throughput	5.1-5.4,5.7,5.8	
F	Fuel type	5.9	
C	Catalyst type	5.11	
N	NH_3 concentration	5.12	Lean stoichiometry, variable NH_3 concentration
D	Dopant type	5.13	Lean stoichiometry, varying with range of temperatures

5.1 SCREENING TEST RESULTS

In this section, the results of the screening tests are presented and discussed. For convenience of discussion the term XN will represent the sum of NO_x and its precursors NH_3 and HCN under fuel-rich and stoichiometric conditions, and only NO_x emissions under fuel-lean conditions. Chemically bound nitrogen content will be presented in terms of weight percent of the fuel and in ppmv when quantitatively converted to NO_x in a product gas from stoichiometric combustion of the fuel in air and without diluent. The screening test data are presented in Appendix A. The NO_x, HCN, and NH_3 emissions data were reduced in terms of percent NH_3 conversion, and are presented in Appendix B. By comparing the emission characteristics of these data, the effects of the screening parameters on the chemically bound nitrogen conversion process were assessed and are discussed in the following subsections.

5.1.1 Bed Temperature Effects on Chemically Bound Nitrogen Conversion

Three series of tests were performed to study the bed temperature effects on chemically bound nitrogen conversion. The first two series of tests were performed using the UOP-1 catalyst at fuel throughputs corresponding to heating potentials of 25.3 MJ/hr (24,000 Btu/hr) and 42.2 MJ/hr (40,000 Btu/hr), and the third series was performed using an Acurex Pt catalyst at a fuel throughput corresponding to a heating potential of 25.3 MJ/hr. Each series involved a full range of fuel/air ratios at each of two bed temperatures (1367K and 1478K). These tests are symbolized with a "T" in Table 5-1.

Figure 5-1 shows the result of natural gas combustion at a fuel throughput of 42.2 MJ/hr (40,000 Btu/hr) and with a chemically bound nitrogen content of 0.3 weight percent in the fuel (equivalent to 307 ppmv when quantitatively converted to NO_x in a product gas from stoichiometric combustion of the fuel in air without diluent). The two bed temperatures evaluated were 1367K (2000°F) and 1478K (2200°F). Under rich test conditions, only small temperature effects were observed. For lean conditions, the data show increased bed temperature results in increased NO_x emissions, with the exception of the somewhat anomalous point at 180 percent theoretical air.

Figure 5-2 shows the results obtained with the same UOP-1 catalyst at a lower fuel throughput, i.e., 25.3 MJ/hr (24,000 Btu/hr), and at a slightly higher nitrogen content (0.5 percent) when compared to the previous case. An

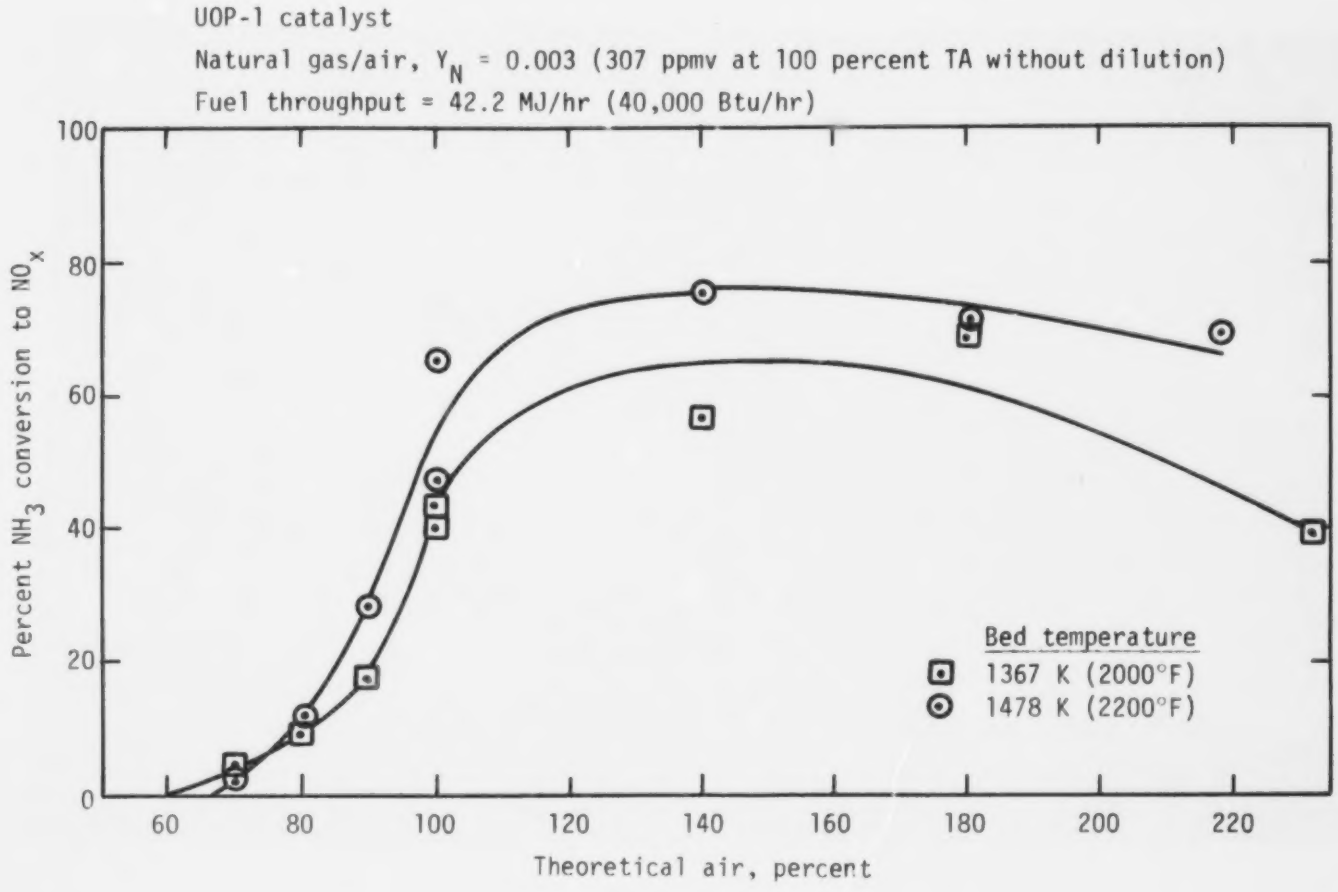


Figure 5-1. Effect of bed temperature on NH_3 conversion to NO_x, UOP-1 catalyst.

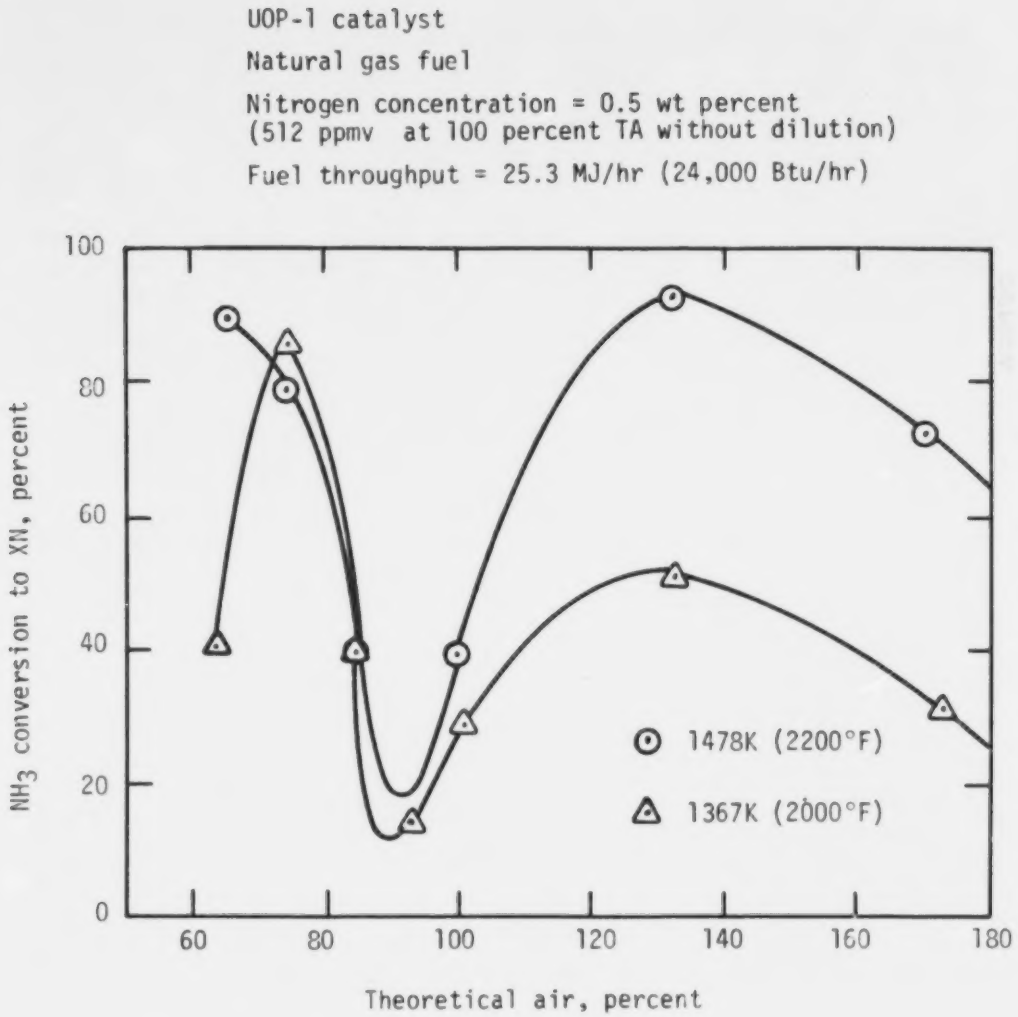


Figure 5-2. Effect of bed temperature on NH_3 conversion to NH_3 + HCN + NO_x, UOP-1 catalyst.

increase in XN emissions as a result of increasing bed temperature under lean conditions was again observed. Under fuel-rich coniditions, the effect of bed temperature on XN emissions was found to be insignificant, except for conditions richer than 65 percent theoretical air. Under these very rich conditions, lower bed temperature resulted in lower XN emissions.

The NH_3 and HCN emissions measured under fuel-rich conditions are given in Figures B-3 and B-4, respectively, for the 1367K (2000°F) and 1478K (2200°F) cases. At 1367K (2000°F), measured NH_3 emissions in the exhaust gas were 20 percent of the dopant at 65 percent theoretical air, increasing to 75 percent at 75 percent theoretical air and then decreasing rapidly as stoichiometric conditions were approached. The HCN emissions decreased monotonically as combustion conditions varied from fuel-rich to stoichiometric. In contrast to the 1367K (2000°F) case, at 1478K (2200°F) the relative emissions of NH_3 and HCN were reversed. Quantitatively, the measured HCN emissions were higher at 1478K (2200°F) than at 1367K (2000°F), with the opposite being true for the NH_3 emissions except at 65 percent theoretical air. If NH_3, HCN, NO_x, and N_2 are assumed to be the primary nitrogenous species formed under fuel-rich conditions, the condition which yields the highest percent of N_2 can be determined by summing the percent yields of NH_3, HCN, and NO_x, and plotting the sum as a function of theoretical air. This condition was found to be at 90 percent theoretical air for both cases. For the 1367K case, there appeared to be a second maximum for N_2 emissions at conditions richer than 65 percent theoretical air (see Figure 5-2).

Figure 5-3 shows the effects of bed temperature and fuel throughput on CO emissions under fuel-lean conditions for the UOP-1 catalyst. The results of the 1478K (2200°F) cases show that CO emissions were maximized at stoichiometric conditions and then decreased to a level below 100 ppmv under fuel-lean conditions. A negligible effect of mass throughput on CO emissions was observed, except at stoichiometric conditions, where an increase in mass throughput resulted in somewhat lower CO emissions. One possible explanation is that the higher mass throughput, and hence higher total heat release, could reduce the heat loss effect, thereby minimizing cold spots at the periphery of the catalytic reactor where the CO oxidation reaction is inhibited due to low temperatures.

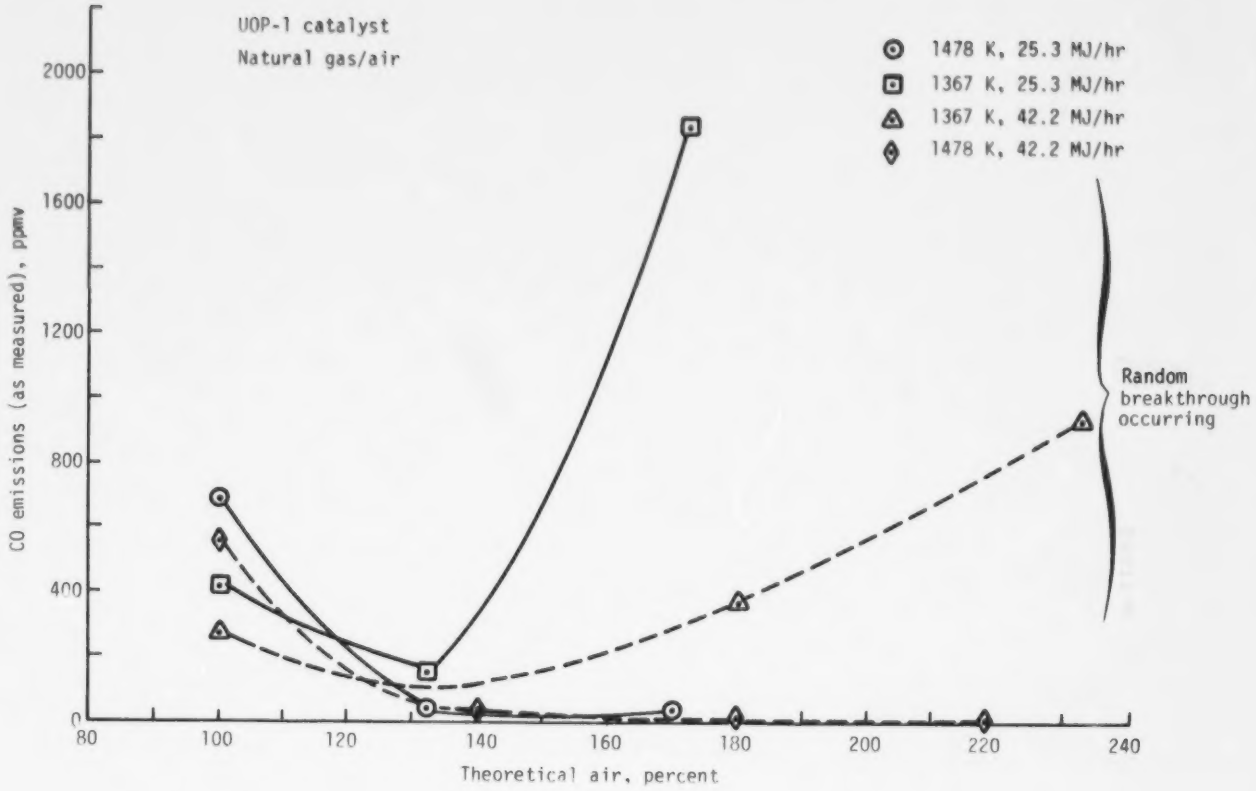


Figure 5-3. CO concentration versus theoretical air, UOP-1 catalyst.

The results of the 1367K (2000°F) cases show that CO emissions were highest on the fuel-lean side instead of at stoichiometric conditions, as in the previous cases. CO emissions initially decreased with increasing theoretical air, and reached a minimum at 130 percent theoretical air. The CO emissions then increased with increasing theoretical air, an apparent effect of total mass throughput on CO emissions (causing the onset of CO breakthrough). An increase in fuel throughput appeared to produce no definable effect on lean CO emissions once CO breakthrough was initiated (CO > 300 ppm). The high CO emissions under fuel-lean conditions at reduced bed temperature are due to the occurrence of CO breakthrough.

In examining the emissions data, some trends indicating possible interactions between fuel NO_x and CO were observed under fuel-lean conditions. It was noted that NO_x emissions decreased as CO concentration increased. These trends are illustrated in Figure 5-4 showing the relationships of NO_x to CO at greater than 130 percent theoretical air. A drop in XN species with increasing CO is noted.

Figure 5-5 shows the effects of bed temperature on the conversion of chemically bound nitrogen using an Acurex platinum catalyst. At a fuel throughput of 42.2 MJ/hr (40,000 Btu/hr), propane was combusted with 2 percent NH_3 by weight (1934 ppmv burned equivalent). The two bed temperatures evaluated were 1367K (2000°F) and 1478K (2200°F). Figure 5-5 shows negligible effect on XN emissions as a result of changes in bed temperature under fuel-lean conditions. XN emissions, however, are higher than those shown in Figure 5-2.* Under fuel-rich and stoichiometric conditions, significant bed temperature effects on XN emissions were observed. Increasing bed temperature resulted in a shifting of the XN minimum towards the stoichiometric condition and an increase in the minimum from 40 to 80 percent conversion. In terms of nitrogenous species constituents, HCN and NH_3 emissions increase as the bed temperature increases, with an opposite influence on NO_x emissions (see Figures B-8 and B-9).

---

*Values in excess of 100 percent are due in part to an approximate 10 percent correction for H_2O condensation which was not included in the screening data reduction.

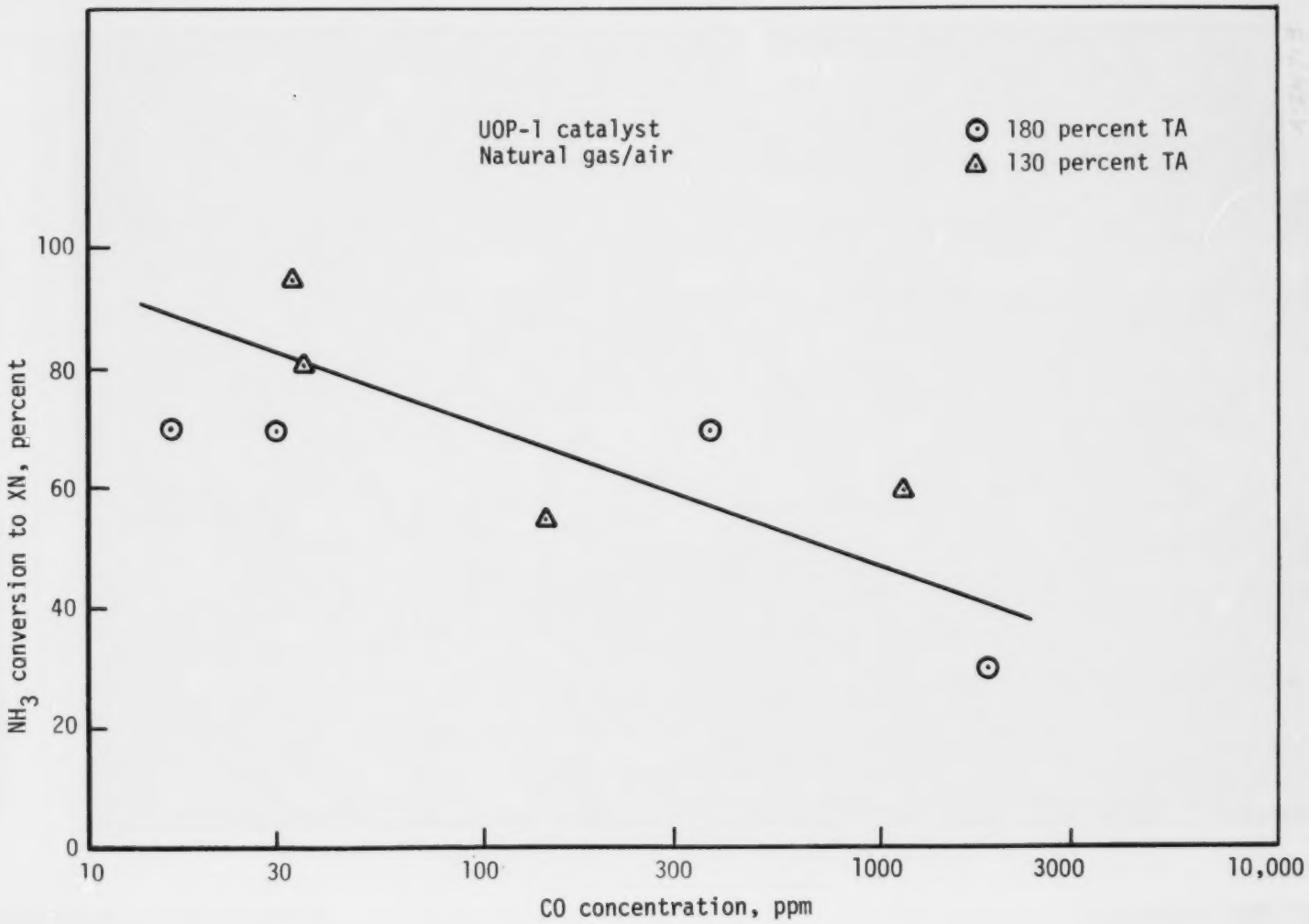


Figure 5-4. Effect of CO on NH_3 conversion to NO_x, UOP-1 catalyst.

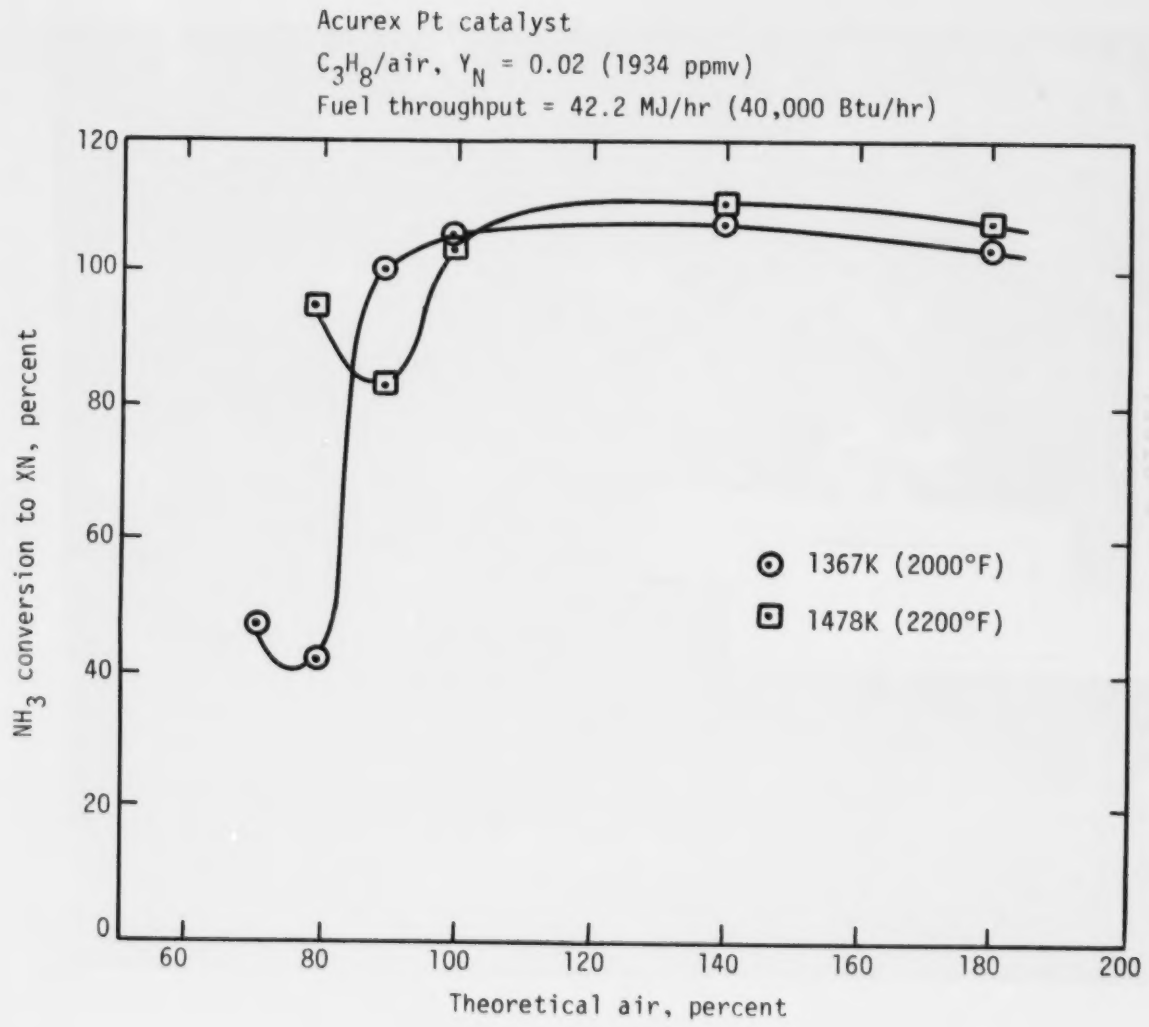


Figure 5-5. Effect of temperature on NH_3 conversion to XN, Acurex Pt catalyst.

Figure 5-6 presents CO and UHC emissions data for the Acurex platinum catalyst. Under fuel-lean conditions (>130 percent theoretical air), CO emissions for both bed temperatures are below 100 ppmv and are nearly identical. At stoichiometric conditions, the CO emissions for the 1478K (2200°F) case increased rapidly to a value exceeding 2000 ppmv, whereas for the 1367K (2000°F) case, CO emissions increased moderately to 200 ppmv. No UHC emissions were observed under fuel-lean conditions. At stoichiometric and fuel-rich conditions, UHC emissions increased with decreasing theoretical air. The 1478K (2200°F) case had lower UHC emissions than the 1367K (2000°F) case, indicating more UHC had been oxidized to form CO at the higher bed temperature. With this catalyst/fuel system no CO breakthrough occurred at 2000°F under lean conditions. Consistent with this result, high conversion of NH_3 to NO_x is observed under all measured lean conditions.

5.1.2 Fuel Throughput Effect on Chemically Bound Nitrogen Conversion

The effect of fuel throughput on the conversion of chemically bound nitrogen was studied by testing the UOP catalysts (UOP-1 and UOP-2) and an Acurex NiO/Pt catalyst with propane, air, and ammonia at fuel throughputs of 25.3 MJ/hr (24,000 Btu/hr) and 42.2 MJ/hr (40,000 Btu/hr). The UOP catalysts were maintained at 1478K (2200°F) during combustion, and the Acurex NiO/Pt catalyst, at 1589K (2400°F), which is the minimum reaction temperature required for this catalyst. The amount of ammonia dopant used was 0.5 percent by weight of the fuel (485 ppmv) for the UOP catalyst tests and 2.0 percent (1934 ppmv) for the Acurex NiO/Pt catalyst tests.* The results of these tests are described below.

Figure 5-7 shows the results of NH_3 conversion to fuel NO_x in the UOP catalysts. Under fuel-lean and stoichiometric conditions, increases in fuel throughput resulted in no significant change in XN emissions. Under fuel-rich conditions, increases in fuel throughput appeared to slightly broaden the XN minimum. This broadening of the XN minimum was caused by simultaneous decreases in both NH_3 and HCN emissions (see Figures B-5 and B-7).

*The increase in NH_3 dopant concentration was prompted by a desire for larger concentrations for specific ion electrode determination.

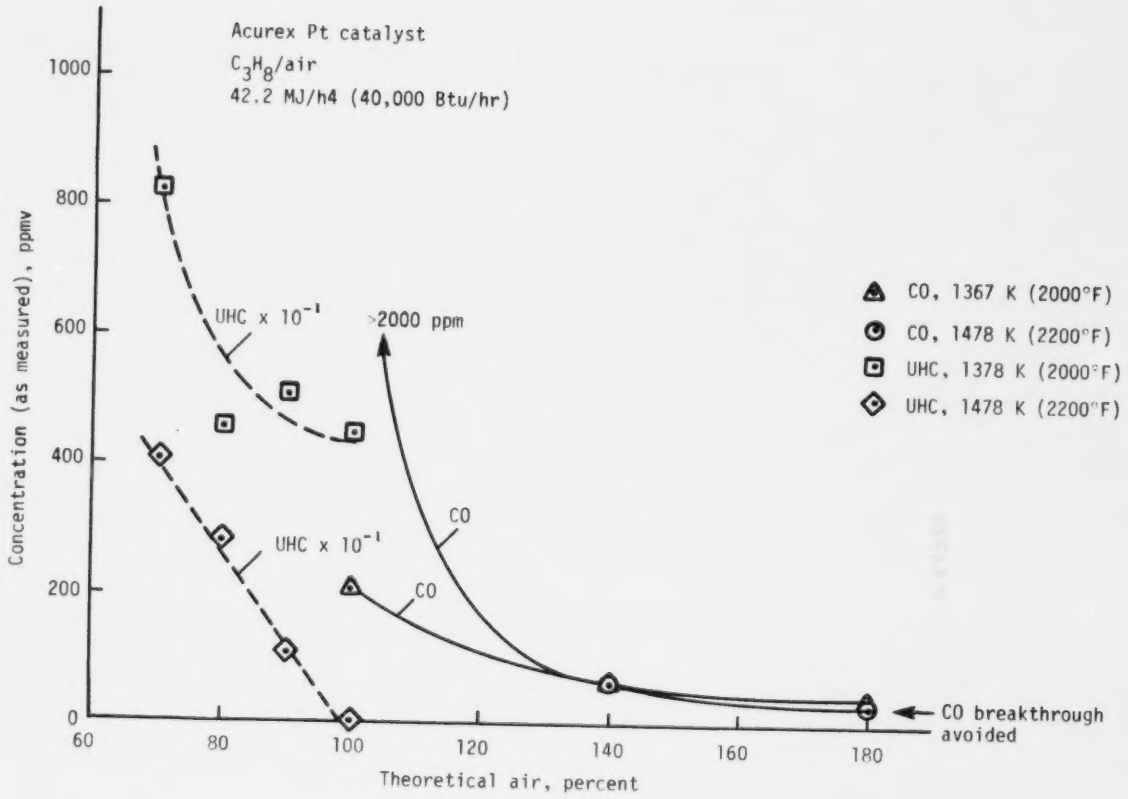


Figure 5-6. CO and UHC emissions versus theoretical air, Acurex Pt catalyst.

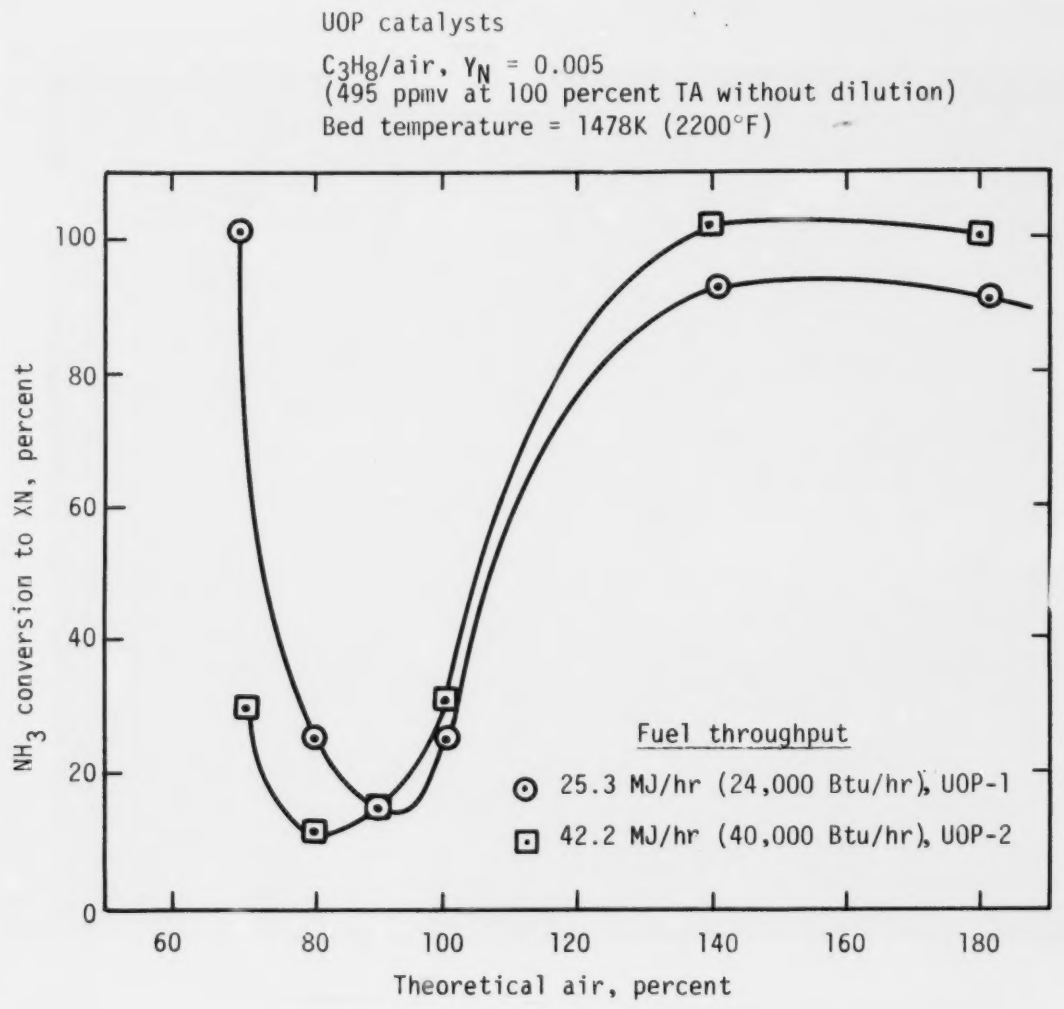


Figure 5-7. Effects of fuel throughput on NH_3 conversion to XN at 1478K, UOP catalysts.

Figure 5-8 shows the results of NH_3 conversion to XN in the Acurex NiO/Pt catalyst. As with the UOP catalyst, increased fuel throughput resulted in no significant change in NO_x emissions under fuel-lean conditions. Under fuel-rich conditions, however, increased mass throughput broadened the fuel NO_x minimum, consistent with the UOP catalyst results. It is also of interest to note the occurrence of a second XN minimum under rich conditions at low fuel throughput.

5.1.3 Fuel Type Effects on Chemically Bound Nitrogen Conversion

Natural gas and propane were used to study the effects of fuel type on the conversion of chemically bound nitrogen in the UOP-1 catalyst. The catalyst temperature was maintained at 1478K (2200°F) with a fuel throughput of 25.3 MJ/hr (24,000 Btu/hr). The amount of ammonia dopant was 0.5 percent by weight of the fuel. The effects of these two fuels on the conversion of NH_3 to fuel NO_x are shown in Figure 5-9.

No significant variations on XN emissions characteristics were observed as a result of changing fuels. Under fuel-lean conditions with natural gas, XN emissions appeared to maximize at 130 percent theoretical air and then declined as theoretical air was further increased. For propane, XN emissions also maximized at 130 percent theoretical air but remained relatively constant as theoretical air was increased. Under fuel-rich conditions, both fuels exhibited the characteristic XN minimum. However, the fuel NO_x minimum for propane was broader and slightly deeper than that for natural gas.

Similar phenomena were observed from Myerson's work (Reference 10) in studying the reduction of nitric oxide in combustion effluents by hydrocarbon-oxygen mixtures. In his work, the fuel NO_x reducing abilities of methane, ethane, and isobutylene were evaluated, as shown in Figure 5-10. All three fuels exhibited similar fuel NO_x minima under fuel-rich conditions. Also, an increase in reducing ability and the width of the fuel NO_x minimum with the number of carbon atoms in the hydrocarbon molecule were noted. Operating at almost the same combustion temperature, similar behavior was observed in catalytic combustion with the exception that the required residence time was an order of magnitude lower than that for Myerson's gas phase reactions.

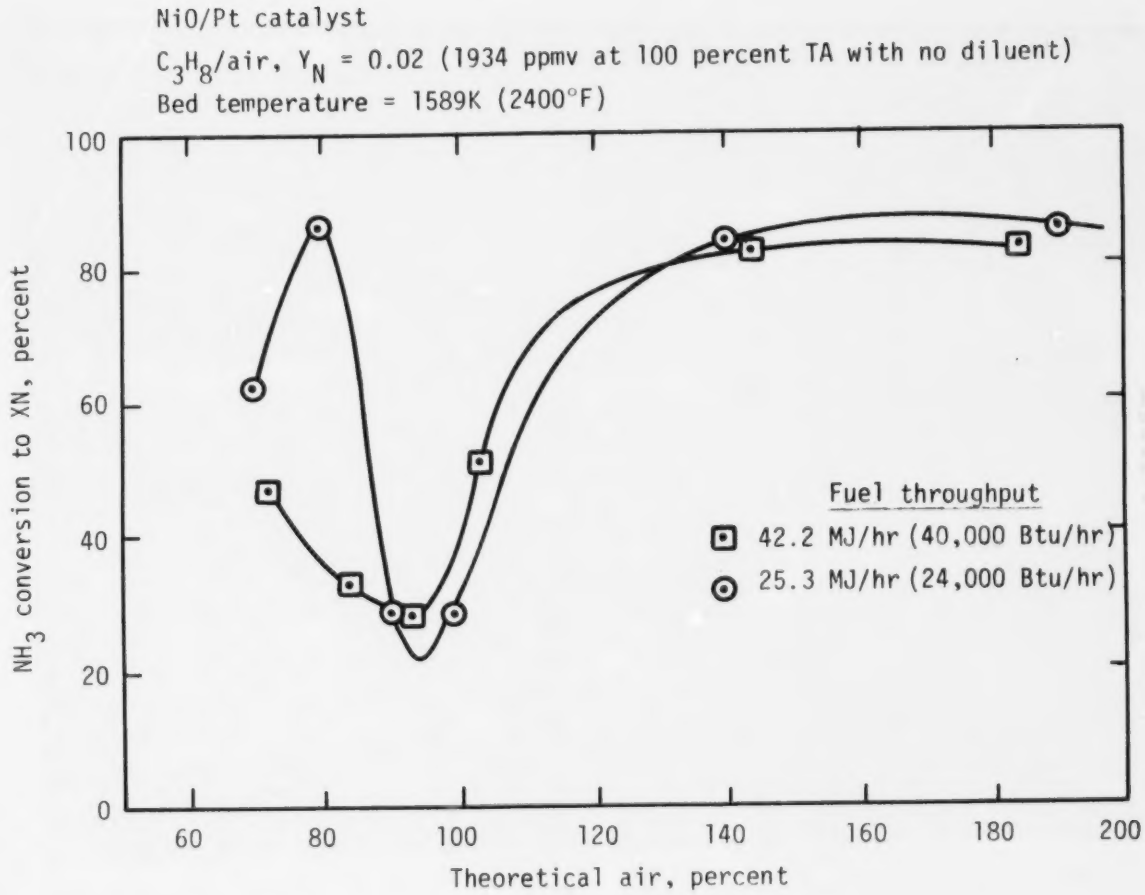


Figure 5-8. Effects of fuel throughput on NH_3 conversion to XN at 1589K, NiO/Pt catalyst.

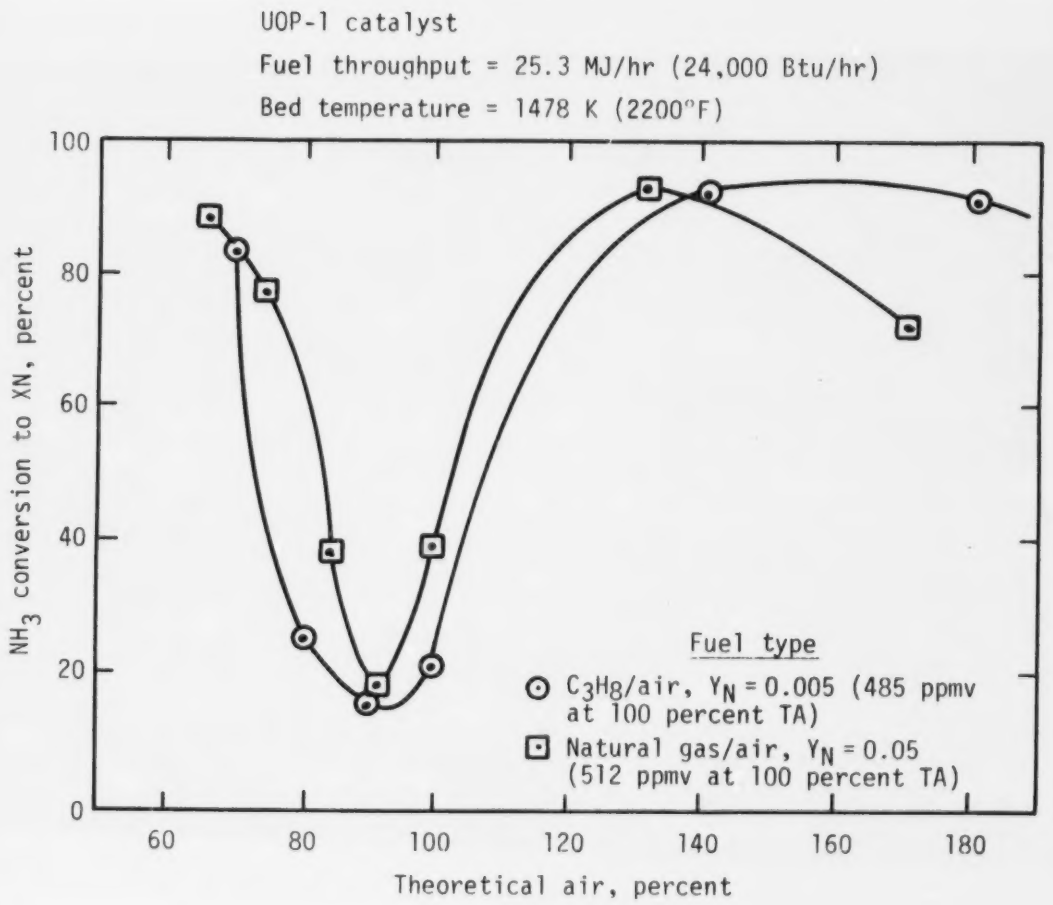


Figure 5-9. Effects of fuel type on NH_3 conversion to XN, UOP-1 catalyst.

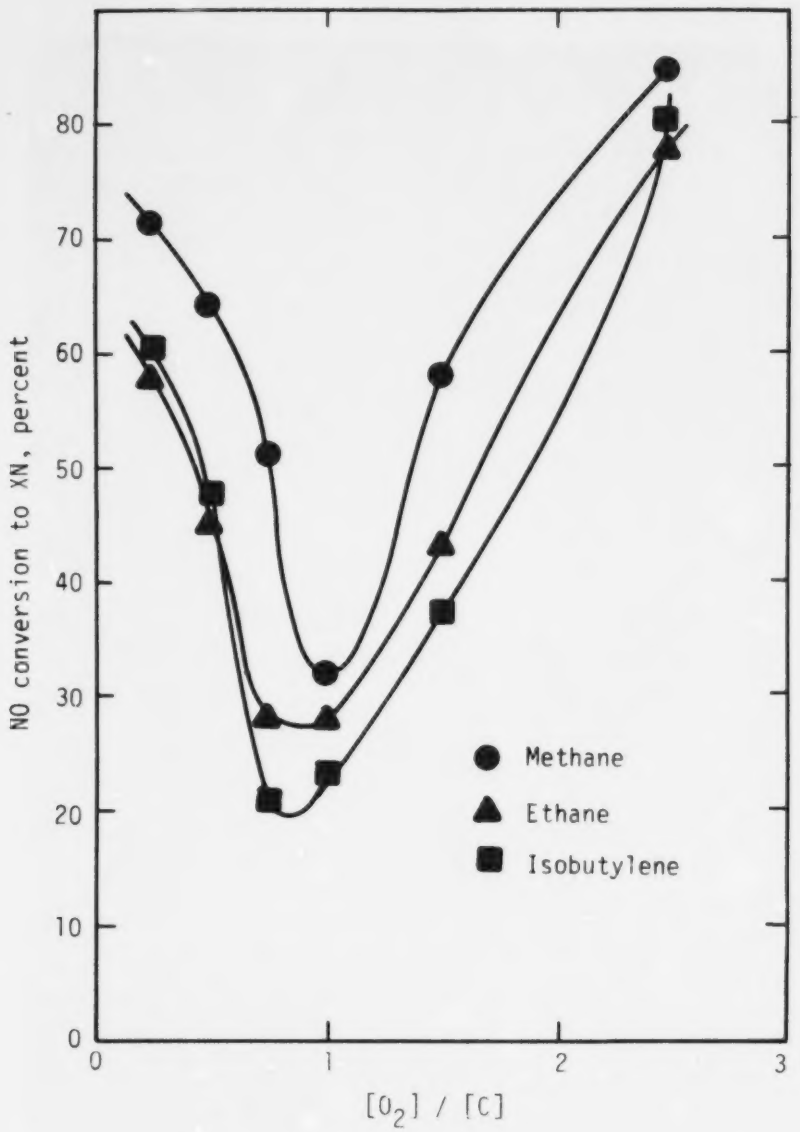


Figure 5-10. Effects of fuel type on NO conversion to NO + HCN + NH_3 in gas phase reactions, temperature = 1423K, τ_{rea} = 189 msec (extracted from Reference 10).

5.1.4 Effect of Catalyst Type on Chemically Bound Nitrogen Conversion

The catalyst type can affect the combustion process in two ways: (1) the hydrocarbon oxidation rate may vary, and (2) the combustion products may vary. These differences can in turn influence the chemically bound nitrogen conversion process, and consequently the XN emissions. To determine these effects, an Acurex platinum catalyst and an Acurex NiO/Pt catalyst were tested. The platinum catalyst had a high activity and required a bed operating temperature of only 1367K (2000°F) for satisfactory combustion efficiency. The NiO/Pt catalyst was not as active, requiring a bed operating temperature of at least 1589K (2400°F) for stable combustion. Since platinum would degrade rapidly at this elevated temperature, the Acurex platinum catalyst was tested only up to 1478K (2200°F).

Although the catalysts were not tested at the same bed temperature, some of the effects of catalyst type on XN formation can be noted from Figure 5-11. The Acurex platinum catalyst results show that 100 percent conversion of NH_3 to NO_x occurred under fuel-lean conditions, and the percent conversion increased slightly with an increase in bed temperature. Under fuel-rich conditions, an increase in bed temperature resulted in an increase in the percent conversion and a shift of the XN minimum towards stoichiometric conditions. Contrary to the trend indicated by the Acurex platinum catalyst results, the XN emissions from the NiO/Pt catalyst were lower even though the bed temperature was higher. However, under rich combustion conditions, the XN minimum shifted towards stoichiometric conditions, as was found for the Acurex platinum catalyst. It should be noted that the UOP catalysts at 2200°F typically showed lean side performance consistent with the NiO/Pt results of Figure 5-11 (see Figures 5-1 and 5-2).

5.1.5 Effect of Chemically Bound Nitrogen Content and Type on its Conversion

The effect of chemically bound nitrogen content at 310 percent theoretical air is shown in Figure 5-12. When the chemically bound nitrogen content was low (<1 percent), almost 100 percent conversion to NO_x was observed. As the chemically bound nitrogen content increased, the percent conversion decreased gradually, reaching a value of 70 percent at a chemically bound nitrogen content of 3.7 percent. Fuel NO_x conversions qualitatively

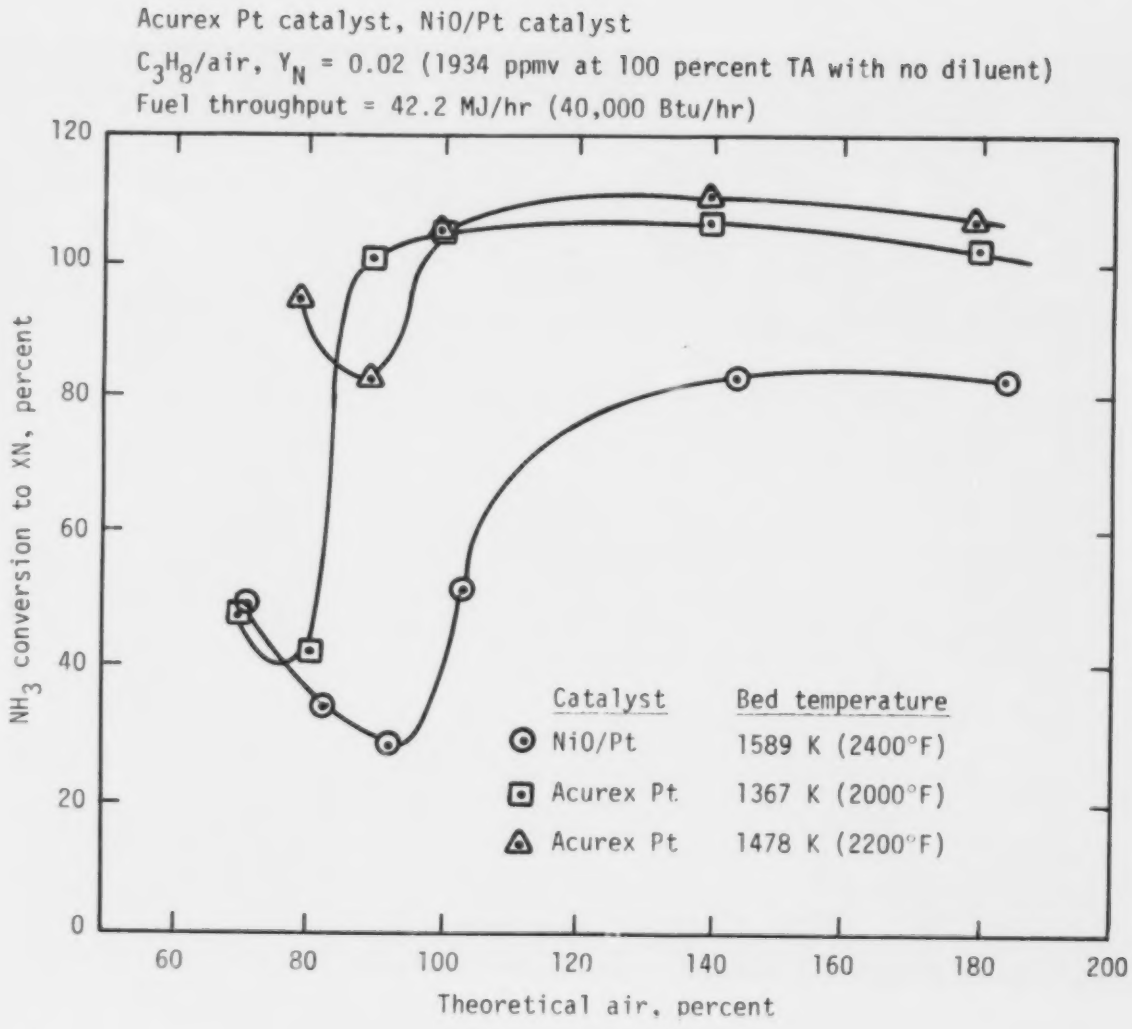


Figure 5-11. Effects of catalyst type on NH_3 conversion to XN, Acurex Pt catalyst and NiO/Pt catalyst.

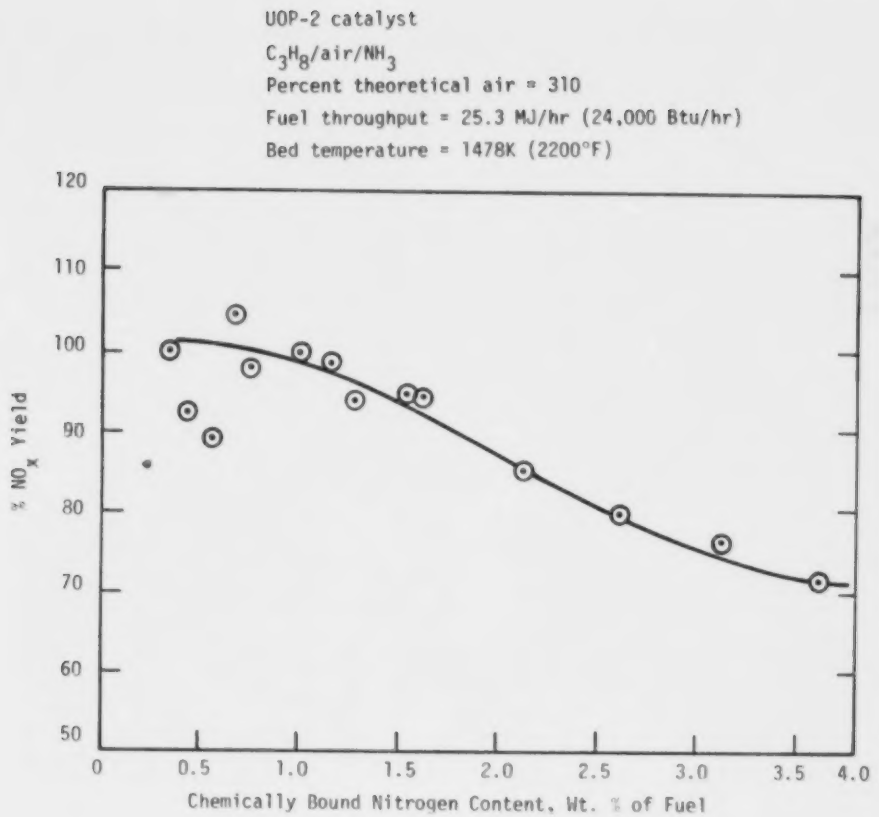


Figure 5-12. Effect of nitrogen content on NO_x emissions, UOP-2 catalyst.

similar to those shown in Figure 5-12 have been observed in conventional combustion studies for both premixed (Reference 4) and diffusional flames (Reference 9). In the premixed flame study, the following two correlations for fuel NO_x emissions were proposed respectively by Fenimore and DeSoete:

$$Y = \frac{X}{(N_f)_o}\left\{1 - \exp\left[-\frac{(N_f)_o}{X}(1 + Y)\right]\right\}$$

$$Y = \frac{2}{1/Y - k_b(N_f)_o/k_a(R)} - 1$$

where Y = fuel NO_x yield, $(N_f)_o$ = total N in the added nitrogen compound, $X = (k_a/k_b)(R)$, R is the oxidant concentration, k_a is the rate constant for $NH_i + R \rightarrow NO$, and k_b is the rate constant for $NH_i + NO \rightarrow N_2$. Both correlations predicted that an increase in the chemically bound nitrogen content could lead to a decrease in fuel NO_x yield for a given stoichiometry, in agreement with the current result. The use of such homogeneous relations to describe what should be a dominantly heterogeneous effect is subject to some interpretation.

The effect of chemically bound nitrogen type on fuel nitrogen conversion to NO_x is shown in Figure 5-13. Methylamine and ammonia were used as the model chemically bound nitrogen compounds in this study. The result shows almost no difference between emissions for the two compounds. This indicates that the pyrolysis kinetics of chemically bound nitrogen from gaseous NH-species may not be significant in the conversion of chemically bound nitrogen to NO_x.

Figure 5-13 also shows the effect of bed temperature on the chemically bound nitrogen conversion under fuel-lean conditions. The bed temperature was varied by maintaining the fuel throughput constant and increasing the air throughput (TA always >250 percent). The fuel NO_x emissions were weakly dependent on bed temperature when the bed temperature was higher than 1400K. As the bed temperature was reduced below 1400K, the fuel NO_x emissions became strongly dependent on bed temperature.

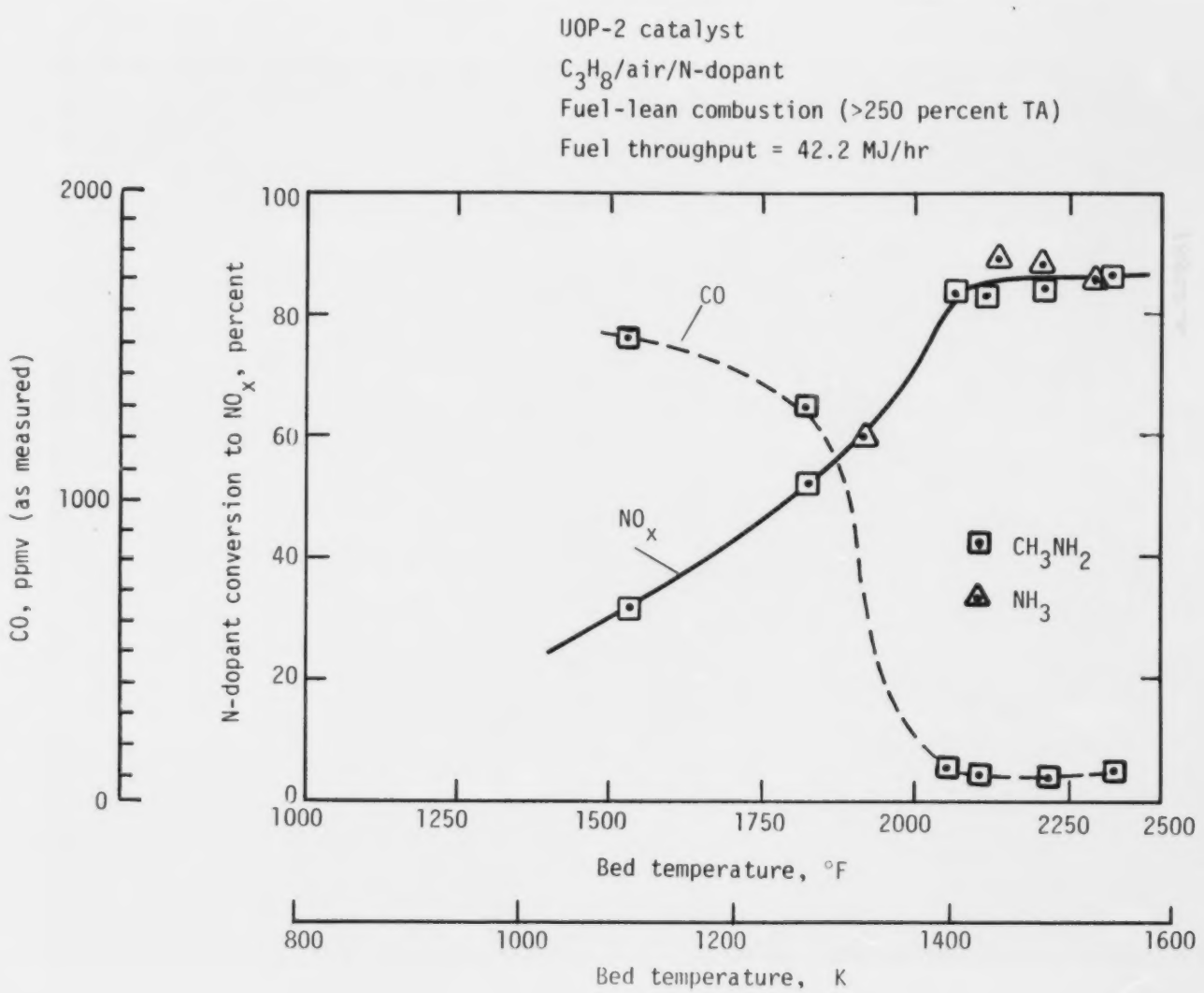


Figure 5-13. Effect of dopant type on NO_x emissions, UOP-2 catalyst.

The corresponding CO emissions are also shown in Figure 5-13. A strong correlation between the NO_x and CO concentrations, as indicated in Section 5.1.1, was observed. This result confirmed that NO_x reduction by CO is possible under fuel-lean conditions. However, the role of the catalyst in fuel NO_x reduction processes may be significant based on a previous study that found that addition of CO caused NO to react catalytically with CO on an iron oxide surface (Reference 11). To determine the effect of the catalyst on this reaction, further study is required.

5.2 DETAILED TEST RESULTS

The results of detailed tests are presented and discussed in this section. The results include the determination of the fate of chemically bound nitrogen during combustion in the UOP-2 catalyst under the following conditions:

- Variable percent theoretical air under fuel-rich and stoichiometric conditions at a fuel nitrogen content of 3 percent by weight of the fuel (2901 ppmv at 100 percent TA with no dilution)
- Same conditions as above but with variable NH_3 concentration

The Acurex Pt and the Acurex NiO/Pt catalysts were also tested in this experimental series, but on a less extensive scale. Only two test conditions were performed with these two catalysts. The first condition was selected at 75 percent theoretical air where N_2 is presumably the major product from the chemically bound nitrogen conversion process. For the other condition, the Acurex Pt catalyst was tested near stoichiometric conditions, and the Acurex NiO/Pt catalyst was tested at 200 percent theoretical air.

The results of detailed tests were summarized and are presented in Appendix A. The gas chromatograph measurements of N_2 concentration are shown in Appendix C.

To assure that the nitrogen species NO_x, N_2, N_2O, HCN, and NH_3 were the dominant products of the chemically bound nitrogen conversion process, a nitrogen mass balance was performed for each test condition. Since the emission data were taken on a dry basis, the following equation was used to account for the water content in the combustion products:

$$Y_{N_o} = (\sum_j N_j) \times (1 - K_{H_2O}) \times 14.007 \times 10^{-6} / \overline{MW}$$

where Y_{N_o} is the total mass fraction of elemental nitrogen in the combustion products, N_j is the ppm of the jth nitrogen species, K_{H_2O} is the mole fraction of water vapor, and $\overline{MW}$ is the mean molecular weight of the combustion products. K_{H_2O} and $\overline{MW}$ were estimated from chemical equilibrium calculations.

The results of the chemically bound nitrogen mass balance are shown in Table 5-2. As may be seen, a maximum deviation of ±13 percent between the input fuel nitrogen content and the measured nitrogen species in the combustion products was obtained, except for Run No. 9 where 17 percent error was observed. This particular test point was repeated in Run No. 12. N_2O was not detected for any test condition. Under fuel-rich conditions, as was expected, N_2 was the dominant product of the chemically bound nitrogen conversion process. Under a fuel-lean condition of 200 percent theoretical air, a conversion of 13 percent NH_3 to N_2 was noted for the NiO/Pt catalyst.

TABLE 5-2. FUEL-N MASS BALANCE

Run No.	Catalyst Type	Fuel-N Content	Theoret. Air	Input Parameters				Mass Fract. of Input Elemental Nitrogen	Nitrogen Species Concentrations in the Combustion Products						Vapor Content	Mean Molecular Weight	Mass Fract. of Output Elemental Nitrogen	Error
		wt (% of fuel)	(%)	C_3H_8 (gm/min)	O_2 (gm/min)	Ar (gm/min)	NH_3 (gm/min)	Y_{N_i} x 10^4	NO (ppm)	$2xN_2$ (ppm)	NH_3 (ppm)	HCN (ppm)	$2xN_2O$ (ppm)	$\Sigma_i N_i$ (ppm)	K_{H_2O} (Mole Fraction)	$\overline{MW}$ (gm/mole)	Y_{N_o} x10^4	(%)
1	Pt	2.0	98	8.482	29.302	768.847	0.203	2.067	455.0	95.64	48.59	7.29	0	694.87	0.0343	39.18	2.069	0.10
2	Pt		77	8.482	23.133	450.875	0.203	3.456	8.0	765.12	174.93	14.58		962.63	0.0259	38.21	3.437	-0.56
3	NiO/Pt		200	12.746	91.264	695.954	0.304	3.126	730.0	119.54	16.40	10.93		876.87	0.0554	38.35	3.026	-3.21
4	NiO/Pt		75	12.746	33.793	486.392	0.304	4.691	125.0	765.12	534.90	40.12		1465.14	0.0308	37.57	5.294	12.86
5	UOP	3.0	100	8.482	29.983	634.038	0.300	3.668	365.0	765.12	51.02	16.28		1197.42	0.0436	39.06	4.107	11.97
6			90	8.482	26.853	587.862	0.300	3.959	12.0	669.48	501.08	30.60		1213.16	0.0346	38.80	4.227	6.81
7			80	11.158	31.253	705.207	0.389	4.280	7.0	956.38	303.53	24.44		1291.35	0.0249	38.49	4.582	7.07
8			75	11.158	29.348	616.711	0.389	4.869	4.0	1338.94	60.88	35.15		1438.97	0.0216	38.19	5.164	6.05
9			70	11.158	27.488	526.762	0.389	5.659	15.50	1163.60	66.66	45.87		1291.63	0.0175	37.80	4.702	-16.91
10		2.4	100	8.482	29.983	682.482	0.253	2.890	200.0	573.84	49.67	6.03		829.54	0.0407	39.12	2.849	-1.43
11		2.0	75	11.158	29.348	616.892	0.278	3.475	2.45	717.30	51.99	22.59		794.33	0.0216	38.22	2.848	-18.02
12		3.6	90	8.482	26.853	585.730	0.389	5.152	10.0	908.56	625.50	69.61		1613.67	0.0347	38.77	5.628	9.23
13		3.0	80	11.158	31.253	469.927	0.389	6.240	57.4	956.32	663.09	293.60		1970.41	0.0356	37.859	7.030	12.66
14	UOP	3.0	70	11.158	27.486	451.129	0.389	6.527	44.0	812.92	747.03	124.81		1728.76	0.0199	37.495	6.330	-3.02

SECTION 6

CONCLUSIONS AND RECOMMENDATIONS

As a result of the experimental study described in this report, an improved understanding of fuel NO_x formation during catalytic combustion has been gained. Knowledge gained in this report may lead to further development of catalytic burners which control both thermal and fuel NO_x. One feasible concept which was demonstrated in Reference 1 and further verified by the present study is the two-stage catalytic combustion system. Also, data obtained under the present study indicate that the design of a lean low NO_x combustor may be possible. This section summarizes the conclusions reached and the concepts formulated under this study, and makes recommendations for further study.

6.1 CONCLUSIONS

Based upon the results of the screening tests, the bed operating temperature was shown to have only a slight effect on fuel NO_x emissions. Under fuel-lean conditions, the bed operating temperature affected fuel NO_x emissions indirectly, depending on the CO emissions and the stoichiometry. High CO emissions tended to suppress fuel NO_x emissions, and this effect became less significant as the test condition became leaner. Under fuel-rich conditions, an increase in the bed operating temperature tended to shift the fuel NO_x minimum slightly towards stoichiometric conditions.

The mass throughput was found to have no significant effect on fuel NO_x emissions under fuel-lean conditions. Under fuel-rich conditions, however, an increase in the mass throughput appeared to broaden the fuel NO_x minimum. In addition, a second fuel NO_x minimum was observed for cases where both the mass throughput and the bed operating temperature were low.

No significant effects on fuel NO_x emissions due to the difference in fuel type were observed. Under fuel-lean conditions with natural gas, fuel

NO_x emissions maximized at 130 percent theoretical air and declined slightly as theoretical air was further increased. With propane, fuel NO_x emissions also maximized at the same stoichiometry but remained relatively constant as theoretical air was further increased. Under fuel-rich conditions, the fuel NO_x minimum for propane appeared to be somewhat broader and slightly deeper than that for natural gas.

Fuel NO_x emissions were found to be strongly dependent on the catalyst type -- a more active catalyst results in higher fuel NO_x emissions with other operating parameters held constant. Under rich conditions, the less active NiO/Pt catalyst achieved a conversion of NH_3 of only 25 percent, while the more active Pt catalyst had a conversion of 80 percent.

Fuel NO_x formation was found to be insensitive to the molecular structure of the chemically bound nitrogen compounds tested. This indicates that the pyrolysis process was not the controlling step for fuel NO_x formation provided that the chemically bound nitrogen content is highly volatile.

The percentage of NH_3 conversion to fuel NO_x was found to be inversely proportional to the chemically bound nitrogen content. This phenomenon was probably due to the destruction reaction prompted by the excess NH_3.

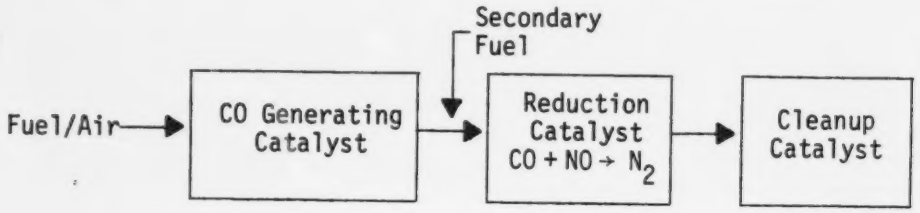
Based upon the results of the detailed tests, it was verified that NO, N_2, NH_3, and HCN are the dominant products of the chemically bound nitrogen conversion process. N_2O was not detected for any condition tested. With the addition of H_2S to the reactive mixture, NO emissions were slightly increased under fuel-rich conditions and inhibited at stoichiometric conditions. A nitrogen balance within reasonable accuracy was not obtained with H_2S addition. The error may be due to the interference of sulfide with the specific ion electrode measurements for HCN and NH_3.

6.2 RECOMMENDATIONS

In order to obtain further understanding of fuel NO_x formation during catalytic combustion, as well as to develop low NO_x combustors, the following studies are recommended:

- A study of CO-NO-catalyst reactions under fuel-lean conditions
- Test of fuels which contain chemically bound nitrogen -- especially those which contain refractory chemically bound nitrogen

- A study of NO_x-SO_x interactions during catalytic combustion for both fuel-rich and fuel-lean conditions
- Development of a lean low NO_x combustor, e.g.,



REFERENCES

1. Kesselring, J. P. et al., "Design Criteria for Stationary Source Catalytic Combustion Systems," Acurex Final Report 78-278, March 1978

2. Matthews, R. D. and Sawyer, R. F., "Fuel Nitrogen Conversion and Catalytic Combustion," University of California/Berkeley, Energy and Environment Division Report LBL-6396, October 1977.

3. Corlett, R. C. and Monteith, L. E., "Fate of Fuel Nitrogen in Backmixed Combustion," Final Report on EPRI Projects RP-241-1 and RP-241-2, Electric Power Research Institute, May 1977.

4. Bowman, C. T., "Kinetics of Pollutant Formation and Destruction in Combustion," Prog. Energy Combustion Science, Vol. 1, 1975.

5. Folsom, B. A. Courtney, C. W., and Heap, M. P., "Environmental Aspects of Low Btu Gas-Fired Catalytic Combustion," Presented at the EPA's Third Workshop on Catalytic Combustion, Asheville, NC, October 1978.

6. Blair, D. W., Bartok, W., Wendt, J. O. L., and Lilley, D. G., "Devolatilization and Pyrolysis of Fuel Nitrogen from Single Coal Particle Combustion," 16th Symposium (International) on Combustion, Boston, Mass., 1976.

7. Seery, J. D., of UTRC, Personal Communication, April 1978.

8. Pershing, D., of the University of Arizona, Personal Communication, April 1978.

9. Fenimore, C. P., "Formation of Nitric Oxide from Fuel Nitrogen in Ethylene Flames," Combustion and Flame, 26, 1972.

10. Myerson, A. L., "The Reduction of NItric Oxide in Simulated Combustion Effluents by Hydrocarbon-Oxygen Mixtures," 15th Symposium (Internal) on Combustion, The Combustion Insitute, 1975.

11. Axworthy, A. W., "Chemistry of Fuel Nitrogen Conversion to Nitrogen Conversion to Nitrogen Oxides in Combustion," EPA-600/2-76-039, February 1978.

12. DeSoete, G., "La Formation des Exyde D'Azote Dans La Zone d'Oxydation des Flammes d'Hydrocarbures," Institute Francais du Petrole, Final Report No. 23309, Ruiell Malmaison, France, June 1975.

13. Wendt, J. O. L., Corley, T. L., and Morcomb, J. T., "Interactions Between Sulfur Oxides and Nitrogen Oxides in Combustion Process," Proceedings of the Second Stationary Source Combustion Symposium, Vol. IV, EPA-600/7-77-073d, July 1977.

14. Kelly, J. T., Kendall, R. M., "Premixed One-Dimensional Flame (PROF) Code Development and Application," Proceedings of the Second Stationary Source Combustion Symposium, Vol. IV, EPA-600/7-77-073d, July 1977.

15. Folsom, B. A. and Courtney, C. W., "Chemiluminescent Measurement of Nitric Oxide in Combustion Products," Proceedings of the Third Stationary Source Combustion Symposium, EPA-600/7-79-056b, February 1979.

APPENDIX A

SUMMARY OF SCREENING AND DETAILED TEST DATA

ACUREX PT CATALYST DATA

Fuel-N Content (% of Fuel)	% TA	Input Gas Mixture Flowrates (SCFM)								Pre-Heat Temp. (°F)	Surface Temperatures						Combustion Products									
		Fuel		Oxidizer		Dilutents		Additives			TC1 (°F)	TC2 (°F)	TC3 (°F)	TC4 (°F)	TC5 (°F)	TC6+ (°F)	CO (PPM)	CO_2 (%)	O_2 (%)	UHC_1 (PPM)	NO (PPM)	N_2 (PPM)	N_2O (PPM)	HCN (PPM)	NH_3 (PPM)	NO_2 (PPM)
		CH_4	C_3H_8	O_2	Air	Ar	N_2	NH_3	H_2S																	
2.0	180	--	.26	--	11.39	--	4.69	.0165	--	579	1649	1964	2194	1595	2191	2186	31.67	5.0	5.88	0	1060	--	--	--	--	20
	140	--	.26	--	8.53	--	7.44	.0165	--	576	1674	1988	2206	1622	2203	2202	63.33	5.1	2.73	0	1100	--	--	--	--	0
	100	--	.26	--	6.33	--	10.04	.0165	--	576	1701	2014	2012	1650	2012	2052	<2000	4.5	0	65.0	730	--	--	--	--	20
	90	--	.26	--	5.69	--	9.78	.0165	--	567	1823	2134	2203	1771	2173	1995	>2000	3.6	0.21	1100	235	--	--	300.63	475.55	--
	80	--	.26	--	5.12	--	7.21	.0165	--	568	2063	2262	2212	2013	2173	2036	>2000	2.8	0.42	2800	38	--	--	364.40	847.85	--
	70	--	.26	--	4.44	--	4.74	.0165	--	547	2110	2263	2152	2082	2120	2012	>2000	2.3	0.84	4100	6	--	--	770.11	1651.96	--
	300	--	.26	--	18.53	--	0.00	.0165	--	556	1448	1726	1922	1323	1920	1798	41.67	4.4	13.34	0	860	--	--	--	--	0
	180	--	.26	--	11.39	--	6.65	.0165	--	566	1508	1792	1999	1416	1990	1877	66.67	4.4	4.83	0	915	--	--	--	--	0
	140	--	.26	--	8.53	--	9.71	.0165	--	558	1536	1819	2005	1472	2010	1872	210	4.5	2.00	0	930	--	--	--	--	15
	100	--	.26	--	6.33	--	12.40	.0165	--	549	1546	1829	2006	1485	2008	1783	1320	3.0	1.89	4500	860	--	--	--	--	5
	90	--	.26	--	5.69	--	12.57	.0165	--	557	1579	1861	2004	1518	1995	1784	>2000	3.0	1.47	5100	840	--	--	26.03	137.24	0
	80	--	.26	--	5.12	--	10.34	.0165	--	576	1820	2041	2010	1756	1979	1832	>2000	2.6	0.63	4600	185	--	--	87.46	155.96	--
	70	--	.26	--	4.44	--	7.49	.0165	--	560	1861	2001	1918	1812	1883	1810	>2000	1.6	0.84	8250	3.5	--	--	234.10	415.20	--
	97.5	--	.16	.78	--	16.36	--	.010	--	572	2170	2300	2200	2260	2142	1800	1900	1.5	--*	2500	455	47.82	0	<7.29	48.59	0
	77.0	--	.16	.616	--	9.59	--	.010	--	573	2112	2169	2050	2166	2054	1856	>2000	1.0	--*	3500	8.0	382.56	0	14.58	174.93	0

T-985

*Malfunction

+TC6 = Exhaust Gas Temperature

ACUREX NiO/Pt CATALYST DATA

Fuel-N Content (% of Fuel)	% TA	Input Gas Mixture Flowrates (SCFM)								Pre-Heat Temp. (°F)	Surface Temperatures						Combustion Products									
		Fuel		Oxidizer		Dilutents		Additives																		
		CH_4	C_3H_8	O_2	Air	Ar	N_2	NH_3	H_2S		TC1 (°F)	TC2 (°F)	TC3 (°F)	TC4 (°F)	TC5 (°F)	TC6* (°F)	CO (PPM)	CO_2 (%)	O_2 (%)	UHC (PPM)	NO (PPM)	N_2 (PPM)	N_2O (PPM)	HCN (PPM)	NH_3 (PPM)	NO_2 (PPM)
2.0	184	--	.24	--	10.48	--	2.98	.015	--	532	2286	2266	2467	--	2336	1967	61.67	6.2	8.82	--	900	--	--	--	--	0
	144	--		--	8.15	--	4.62		--	542	2325	2373	2546	--	2360	1846	236.67	6.8	5.57	--	950	--	--	--	--	50
	103	--		--	5.88	--	4.63		--	601	2432	2335	2445	--	2477	2214	>500	5.2	4.62	--	720	--	--	--	--	0
	92	--		--	5.25	--	3.56		--	652	2246	1932	2120	--	2282	1960		3.4	1.68	2200	310	--	--	267.86	43.73	--
	82	--		--	4.65	--	4.61		--	664	2250	2063	2620	--	2182	1973		1.2	3.15	16500	86	--	--	49.29	98.58	--
	71	--		--	4.07	--	3.09		--	653	2260	2245	2440	--	2286	2144		1.6	1.26	8000	38	--	--	829.15	119.71	--
	180	--	.16	--	6.83	--	2.83	.010	--	622	2316	2420	2630	--	2610	1922	200	6.2	8.61	10	875	--	--	--	--	0
	140	--		--	5.12	--	4.04		--	618	2368	2359	2425	--	2416	1974	480	6.6	4.20	10	900	--	--	--	--	0
	100	--		--	3.81	--	3.00		--	592	2355	2310	2480	--	2280	1973	>500	4.5	1.33	1160	365	--	--	--	--	0
	90	--		--	3.42	--	3.09		--	610	2302	2262	2490	--	2510	1940		1.5	4.41	16000	260	--	--	57.63	801.69	--
	80	--		--	3.06	--	3.36		--	623	2218	2230	--	--	2480	2042		1.8	2.31	14750	48	--	--	67.48	1204.56	--
	70	--		--	2.66	--	2.22		--	692	2244	2302	--	--	2345	1992		1.6	1.47	5000	12	--	--	131.19	460.97	--
	200	--	.24	2.43	--	14.81	--	.015	--	583	2210	2320	--	--	2200	1097	20	1.5	3.15	0	730	59.77	0	10.93	16.40	--
	75	--		0.90	--	10.35	--		--	581	2600	--	1710	--	1780	2029	391.67	--	1.33	15000	125	382.56	0	40.12	534.90	--

*TC6 = Exhaust Gas Temperature

T-985

09

UOP-2 CATALYST DATA

Fuel-N Contents (% of Fuel)	% TA	Input Gas Mixture Flowrates (SCFM)								Preheat Temp (°F)	Surface Temperatures						Combustion Products									
		Fuel		Oxidizer		Dilutents		Additives			TC1	TC2	TC3	TC4	TC5	TC6	CO	CO_2	O_2	UHC	NO	N_2	N_2O	HCN	NH_3	NO_2
		CH_4	C_3H_8	O_2	Air	Ar	N_2	NH_3	H_2S		(°F)	(°F)	(°F)	(°F)	(°F)	(°F)	(PPM)	(%)	(%)	(PPM)	(PPM)	(PPM)	(PPM)	(PPM)	(PPM)	(PPM)
2.0	286	--	0.26	--	18.13	--	0	0.016	--	545	1948	2290	2231	--	--	2167	110.2	5.7	12.51	--	813.5	--	--	--	--	--
	305	--		--	19.29	--			--	534	1844	2200	2132	--	--	2139	102.9	5.4	13.03	--	792.5	--	--	--	--	--
	335	--		--	21.22	--			--	537	1727	2080	2130	--	--	2075	103.5	5.0	13.74	--	726.5	--	--	--	--	--
	350	--		--	22.18	--			--	540	1539	1800	1915	--	--	1862	1372.8	4.1	14.81	--	470	--	--	--	--	--
0.5	180	--		--	11.38	--	7.95	0.0039	--	587	1904	2150	2203	--	--	2198	50.0	6.0	*	0	230	--	--	--	--	--
	140	--		--	8.53	--	10.80		--	587	1931	2168	2206	--	--	2171	700.0	6.0	*	0	230	--	--	--	--	--
	100	--		--	6.33	--	11.52		--	584	2049	2202	2093	--	--	1869	>2000	3.0	*	8,350	68	--	--	--	--	--
	90	--		--	5.70	--	9.66		--	596	2160	2205	2059	--	--	1822	>2000	2.7	*	8,600	15	--	8.80	13.36	--	--
	80	--		--	5.12	--	7.59		--	581	2206	2216	2054	--	--	1909	>2000	2.4	*	7,000	4.3	--	4.86	21.87	--	--
	70	--		--	4.44	--	5.46		--	566	2206	2182	2014	--	--	1922	>2000	2.5	*	7,400	2.8	--	19.55	87.10	--	--
2.0	332	--		--	21.03	--	0	0.019*	--	539	1705	1984	2060	--	--	1989	115.9	5.0	13.70	--	778	--	--	--	--	--
	320	--		--	20.25	--			--	542	1753	2108	2080	--	--	2068	109.0	5.1	13.48	--	795.5	--	--	--	--	--
	308	--		--	19.48	--			--	537	1816	2204	2053	--	--	2109	106.5	5.3	13.18	--	840.0	--	--	--	--	--
	299	--		--	18.90	--			--	534	1912	2315	2050	--	--	2168	109.8	5.6	12.65	--	887.5	--	--	--	--	--
	366	--		--	23.15	--			--	540	1548	1820	1700	--	--	1816	1504.3	4.0	15.07	--	439.5	--	--	--	--	--
	419	--		--	26.51	--			--	537	1068	1529	--	--	--	1059	1372.0	1.0	20.88	--	235.2	--	--	--	--	--
3.0	100	--	0.16	0.799	--	13.492	--	0.0148	--	590	2004	2177	2092	--	--	1742	>2000	1.53	1.00	430	365.00	382.56	0	16.28	51.02	--
	90	--	0.16	0.715	--	12.510	--	0.0148	--	573	1969	2006	1892	--	--	1606		1.02	0.33	5,600	12.00	334.74		30.60	501.08	--
	80	--	0.21	0.832	--	15.007	--	0.0192	--	570	2104	2142	2010	--	--	1687		1.03	1.12	6,900	7.00	478.19		24.44	303.53	--
	75	--		0.782	--	13.124	--		--	582	1952	1981	1889	--	--	1584		0.88	1.03	7,000	4.00	669.47		35.15	60.88	--
	70	--		0.732	--	11.209	--		--	570	1995	2007	1898	--	--	1621		0.80	1.18	8,350	15.50	581.80		45.87	66.66	--
2.0	100	--	0.16	0.799	--	14.523	--	0.0125	--	591	1914	2030	1962	--	--	1625		1.40	0.95	4,850	200.00	286.92		6.03	49.67	--
2.0	75	--	0.21	0.732	--	11.570	--	0.0137	--	574	1992	2013	1931	--	--	1614		0.87	1.25	10,500	1.70	239.10		20.27	47.14	--
4.0	90	--	0.16	0.715	--	12.464	--	0.0192	--	573	1965	1998	1881	--	--	1606		0.97	0.33	5,750	10.00	454.28		69.61	625.50	--
3.0	100	--		0.799	--	12.351	--	0.0148	0.0058	565	2067	2015	1878	--	--	1617		1.22	1.90	6,900	255.00	191.28		94.38	94.75	--
4.0	90	--		0.715	--	10.256	--	0.0192	0.0029	560	2020	2016	1473	--	--	1650		0.40	1.43	7,100	130.00	382.56		120.62	535.67	--
3.0	80	--	0.21	0.832	--	9.559	--		0.0058	548	2145	2096	1866	--	--	1742		0.75	1.95	10,000	44.00	286.92		167.63	430.00	--
	75	--		0.782	--	9.645	--			599	2018	1984	1800	--	--	1712		0.58	1.87	10,700	16.00	167.37		182.55	504.10	--
	70	--		0.732	--	8.049	--			583	2059	2029	1807	--	--	1758		0.43	2.05	12,000	4.40	95.64		248.76	430.98	--
	80	--		0.832	--	10.000	--		--	514	2283	2054	1829	--	--	1713	181.5	--	--	--	57.40	478.16		293.60	663.09	--
	70	--		0.732	--	9.600	--		--	505	2009	1875	1664	--	--	1544	>2000	--	--	--	44.00	406.46		124.81	747.03	--

*Malfunction of O_2 meter

*CH_3NH_2

UOP-1 CATALYST DATA

Fuel-N Content (% of Fuel)	% TA	Input Gas Mixture Flowrates (SCFM)								Pre-Heat Temp. (°F)	Surface Temperatures						Combustion Products									
		Fuel		Oxidizer		Diluents		Additives			TC1 (°F)	TC2 (°F)	TC3 (°F)	TC4 (°F)	TC5 (°F)	TC6* (°F)	CO (PPM)	CO_2 (%)	O_2 (%)	UHC (PPM)	NO (PPM)	N_2 (PPM)	N_2O (PPM)	HCN (PPM)	NH_3 (PPM)	NO_2 (PPM)
		CH_4	C_3H_8	O_2	Air	Ar	N_2	NH_3	H_2S																	
0.5	170	.40	--	--	6.87	--	3.63	.0021	--	613	2070	2189	2200	--	--	1951	29.4	5.1	6.62	--	140	--	--	--	--	0
	132		--	--	5.33	--	5.87		--	611	2083	2200	2206	--	--	1876	31.8	5.1	2.63	--	168	--	--	--	--	0
	100		--	--	4.05	--	8.55		--	610	2076	2192	2201	--	--	1767	684.8	3.5	2.65	--	63	--	--	--	--	0
	93		--	--	3.80	--	7.02		--	608	2045	2171	2200	--	--	1782	>2000	3.4	2.26	--	12.54	--	--	49.12	35.09	--
	84		--	--	3.44	--	5.62		--	599	2042	2164	2200	--	--	1870		4.0	0.32	--	17.63	--	--	101.75	112.28	--
	74		--	--	3.03	--	4.16		--	604	2045	2168	2202	--	--	1950		3.5	0.46	--	7.35	--	--	101.75	203.51	--
	66		--	--	2.68	--	2.90		--	599	2042	2167	2204	--	--	1910		3.2	0.78	--	4.23	--	--	--	--	--
	172		--	--	6.95	--	4.96		--	612	1928	2021	2005	--	--	1646	1834.8	3.6	6.63	--	53.40	--	--	--	--	0
	132		--	--	5.33	--	7.59		--	613	1924	2015	1999	--	--	1598	141.7	2.7	5.16	--	80.70	--	--	--	--	0
	100		--	--	4.05	--	9.63		--	613	1915	2007	1998	--	--	1596	417.9	2.6	2.59	--	43.10	--	--	--	--	0
	93		--	--	3.80	--	9.40		--	611	1884	1982	1997	--	--	1598	>2000	2.5	2.25	--	20.40	--	--	--	--	--
	84		--	--	3.44	--	7.86		--	594	1875	1978	2000	--	--	1693		2.3	1.94	--	13.30	--	--	7.02	42.11	--
	74		--	--	3.03	--	6.16		--	629	1872	1978	2002	--	--	1740		2.1	1.25	--	6.40	--	--	24.65	157.89	--
	66		--	--	2.68	--	4.47		--	619	1866	1972	2002	--	--	1779		2.3	0.71	--	5.60	--	--	59.65	52.63	--
0.3	233	.65	--	--	15.44	--	0		--	630	2026	2037	1549	--	--	1549	927.0	4.2	13.63	--	51.50	--	--	--	--	0
	180		--	--	11.81	--	5.22		--	609	2016	2081	2010	--	--	1777	364.7	4.7	7.54	--	82.00	--	--	--	--	0
	140		--	--	9.21	--	8.56		--	608	2010	2076	2007	--	--	1701	1120.7	4.5	4.09	--	64.40	--	--	--	--	0
	100		--	--	6.62	--	12.83		--	614	1966	2000	1906	--	--	1524	161.7	2.5	4.76	--	42.40	--	--	--	--	0
	100		--	--	6.62	--	12.67		--	595	1997	2064	2000	--	--	1581	265.0	2.6	4.23	--	45.00	--	--	--	--	0
	90		--	--	5.97	--	12.83		--	611	1972	2048	2012	--	--	1633	1842.4	2.5	3.58	--	20.00	--	--	<7.02	< 14.04	--
	80		--	--	5.31	--	10.38		--	--	1953	2035	2026	--	--	--	>2000	2.1	3.10	--	11.70	--	--	<10.53	10.53	--
	70		--	--	4.67	--	8.46		--	619	1930	1998	2004	--	--	1730	>2000	1.4	2.93	--	6.30	--	--	<7.02	<14.04	0
	218		--	--	14.29	--	0		--	638	2146	2203	2180	--	--	1795	4.6	4.5	13.14	--	96.20	--	--	--	--	0
	180		--	--	11.81	--	3.28		--	612	2131	2206	2154	--	--	1962	16.3	5.4	8.75	--	93.90	--	--	--	--	0
	140		--	--	9.21	--	5.98		--	610	2124	2197	2137	--	--	1915	34.5	5.4	5.08	--	99.90	--	--	--	--	0
	100		--	--	6.62	--	10.00		--	610	2130	2200	2137	--	--	1804	556.2	5.1	0.85	--	79.70	--	--	--	--	0
	90		--	--	5.97	--	9.46		--	611	2128	2207	2161	--	--	1732	1550.0	2.85	3.50	--	36.50	--	--	<7.02	38.28	--
	80		--	--	5.31	--	7.49		--	--	--	2200	--	--	--	--	>2000	2.50	3.30	--	18.60	--	--	--	--	--
	70		--	--	4.67	--	5.87		--	594	2110	2202	2199	--	--	1825	>2000	2.20	3.30	--	17.00	--	--	< 7.02	14.04	--
	100		--	--	6.62	--	9.72		--	613	2100	2201	2209	--	--	1934	>2000	1.90	2.20	--	5.30	--	--	<10.53	42.11	--
0.5	180	--	.16	--	6.83	--	3.63	.0023	--	636	2137	2200	2122	--	--	1677	>2000	2.80	4.88	--	58.10	--	--	--	--	0
	140	--		--	5.12	--	6.26		--	616	1879	2077	2200	--	--	2134	46.6	6.3	5.56	--	164.00	--	--	--	--	0
	100	--		--	3.81	--	7.08		--	617	1898	2088	2200	--	--	2152	164.7	6.4	1.27	--	182.40	--	--	--	--	0
0.4	90	--		--	[illegible]	--	5.06	.0018	--	613	1960	2156	2191	--	--	1912	>500	4.4	0.29	--	40.80	--	--	--	--	0
	80	--		--	3.06	--	4.52		--	465	2109	2248	2206	--	--	1904	>2000	4.5	0.41	--	9.80	--	--	59.65	31.58	--
	70	--		--	2.66	--	2.59		--	612	2190	2258	2200	--	--	1927	>2000	3.8	0.62	--	5.30	--	--	38.60	14.04	--
0.3	180	--	.26	--	11.39	--	5.29	.0021	--	584	2231	2285	2207	--	--	1920	>2000	3.7	1.15	--	3.30	--	--	52.63	336.80	--
	140	--		--	8.53	--	8.24		--	606	1907	2088	2204	--	--	2196	58.5	6.8	5.57	--	91.20	--	--	--	--	0
	100	--		--	6.33	--	10.63		--	605	1920	2099	2202	--	--	2205	101.7	6.7	2.60	--	91.40	--	--	--	--	0
	90	--		--	5.69	--	10.27		--	622	1944	2133	2204	--	--	1927	>500	5.8	0.36	--	66.40	--	--	--	--	0
	80	--		--	5.12	--	8.46	.0021	--	620	2025	2201	2200	--	--	1860	>500	3.8	1.92	--	15.00	--	--	7.02	<14.04	--
	70	--		--	4.44	--	5.87		--	610	2165	2255	2202	--	--	1858	>2000	3.6	1.25	--	4.60	--	--	14.04	17.54	--
										596	2213	2207	2200	--	--	1916		3.5	0.85	--	2.20	--	--	7.02	217.54	--

*TC6 = Exhaust Gas Temperature

APPENDIX B

THE CONVERSION OF CHEMICALLY BOUND NITROGEN TO NO_x, NH_3 AND HCN

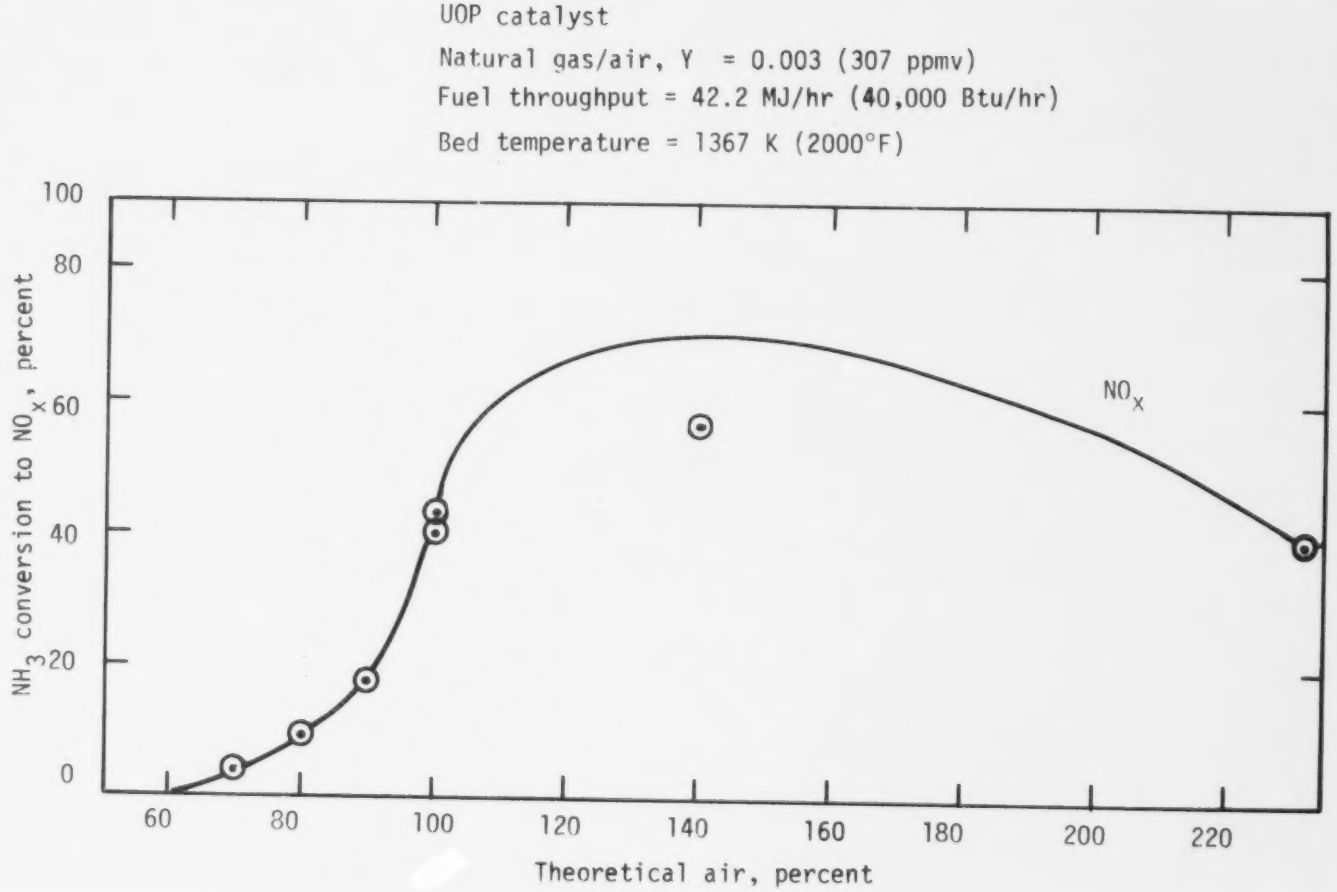


Figure B-1. NH_3 conversion at 1367 K, UOP-1 catalyst.

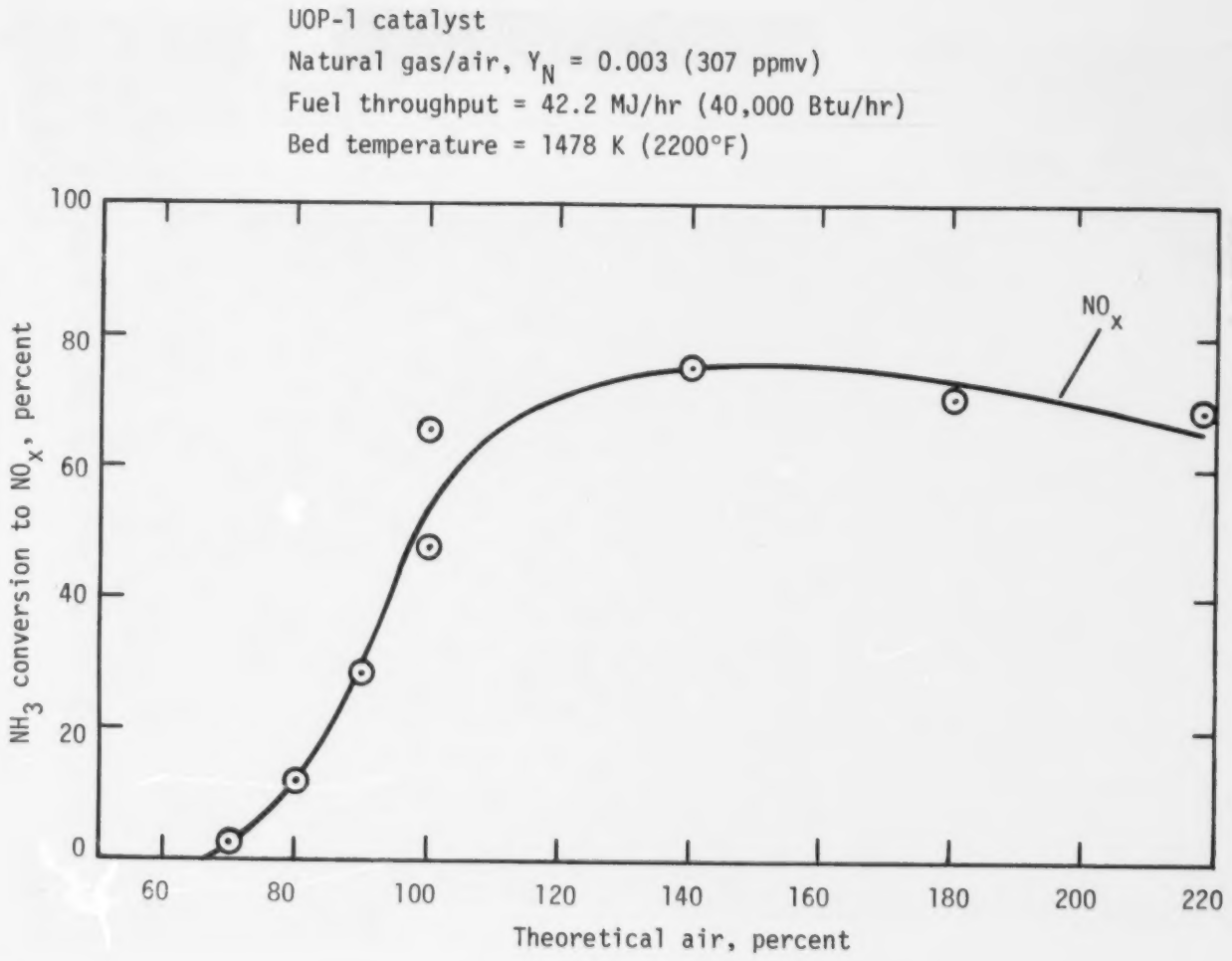


Figure B-2. NH_3 conversion at 1478 K, UOP-1 catalyst.

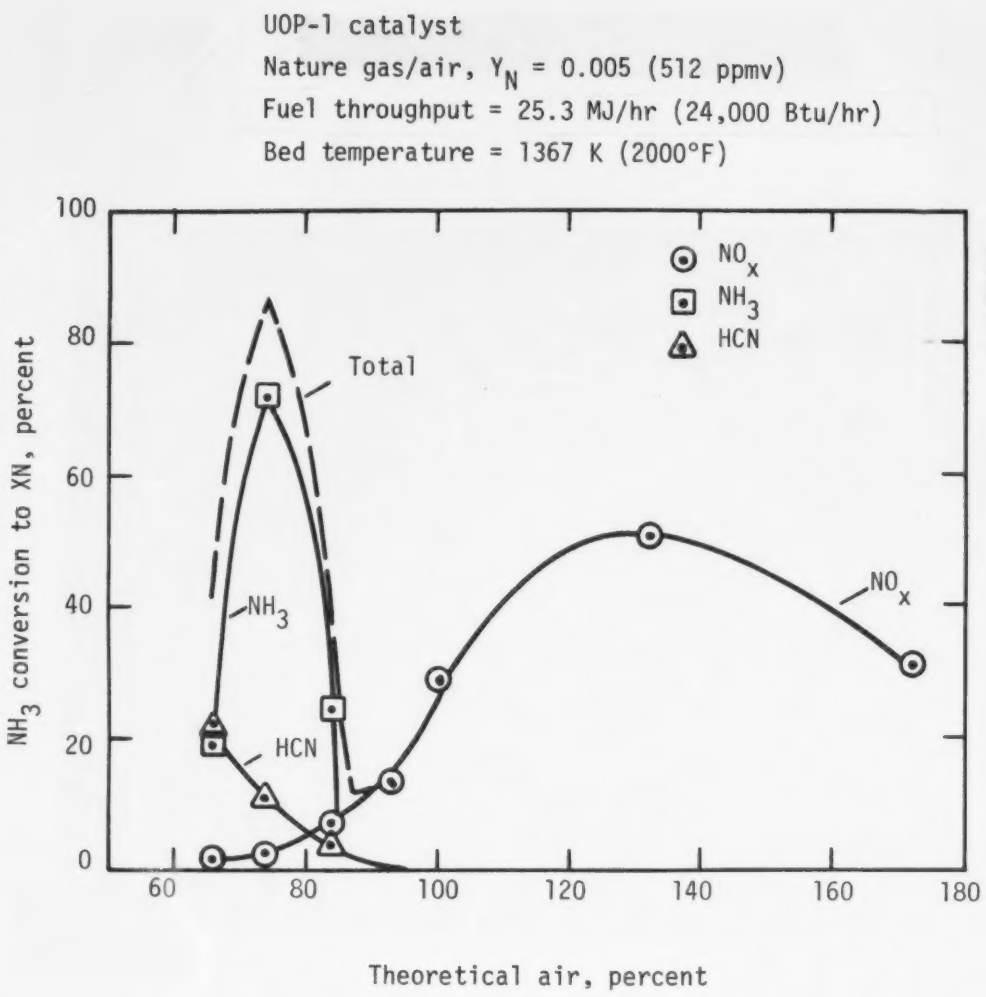


Figure B-3. NH_3 conversion at 1367 K, UOP-1 catalyst.

UOP-1 catalyst
Natural gas/air, Y_N = 0.005 (512 ppmv)
Fuel throughput = 25.3 MJ/hr (24,000 Btu/hr)
Bed temperature = 1478 K (2200°F)

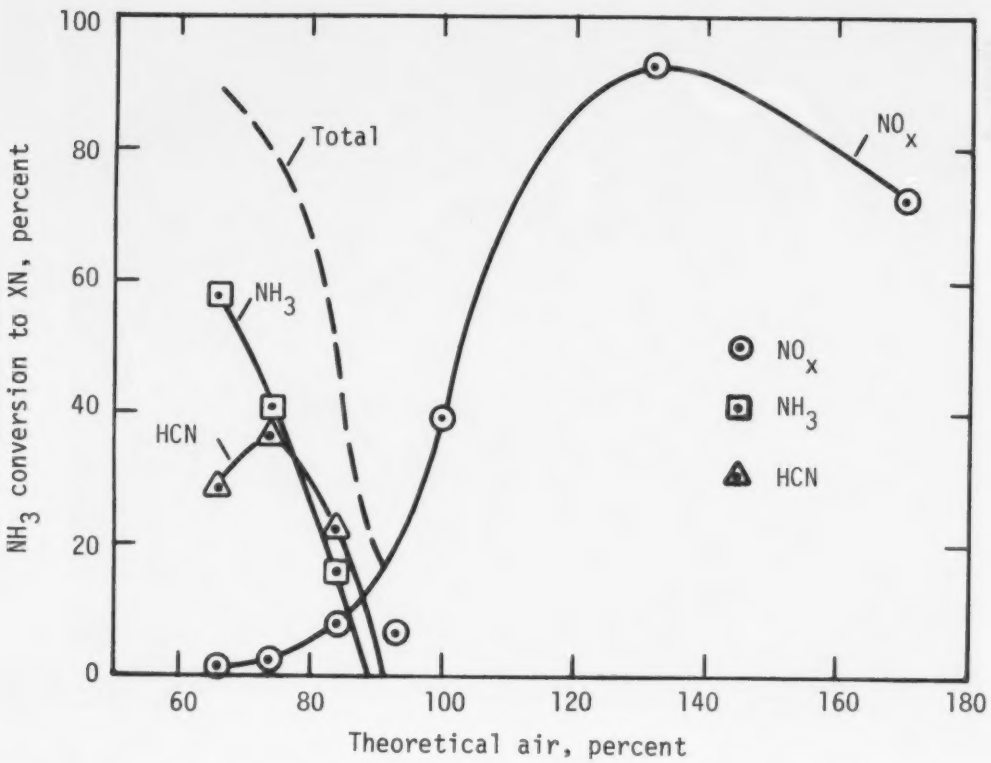


Figure B-4. NH_3 conversion at 1478 K, UOP-1 catalyst.

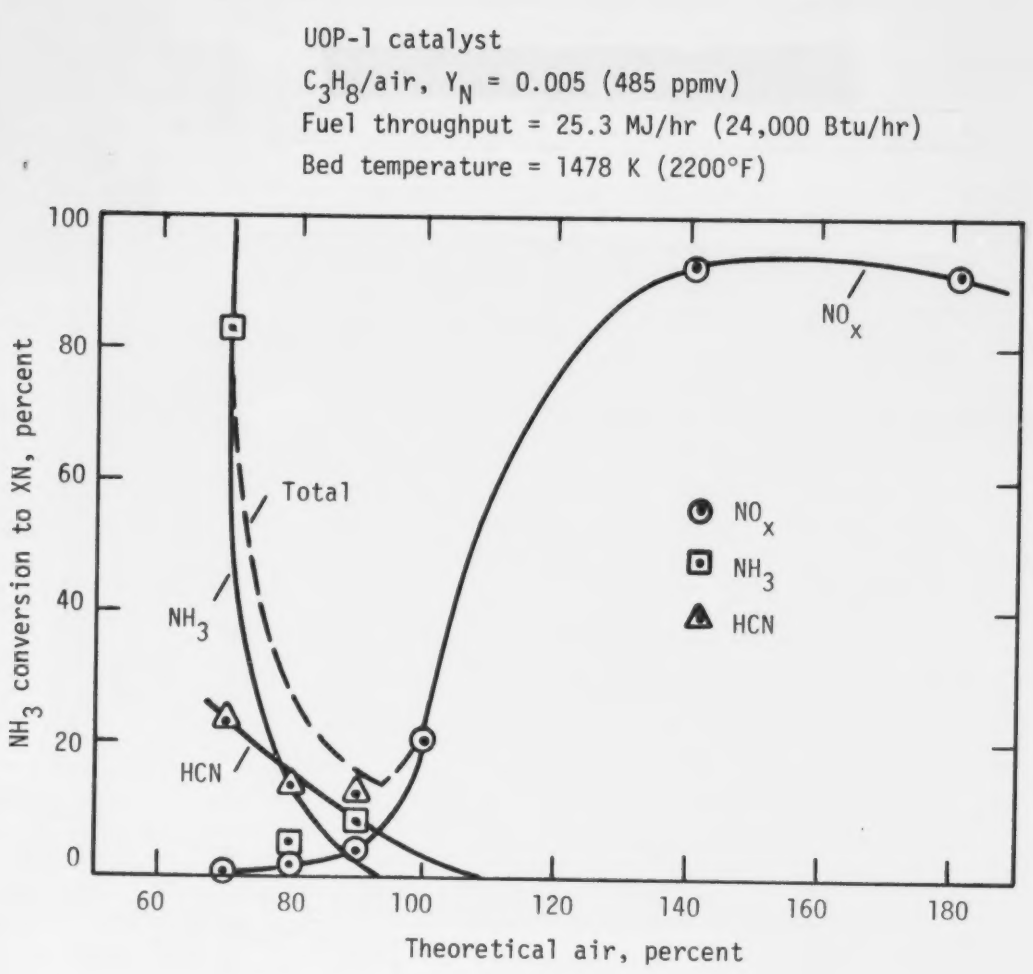


Figure B-5. NH_3 conversion to 1478 K, UOP-1 catalyst.

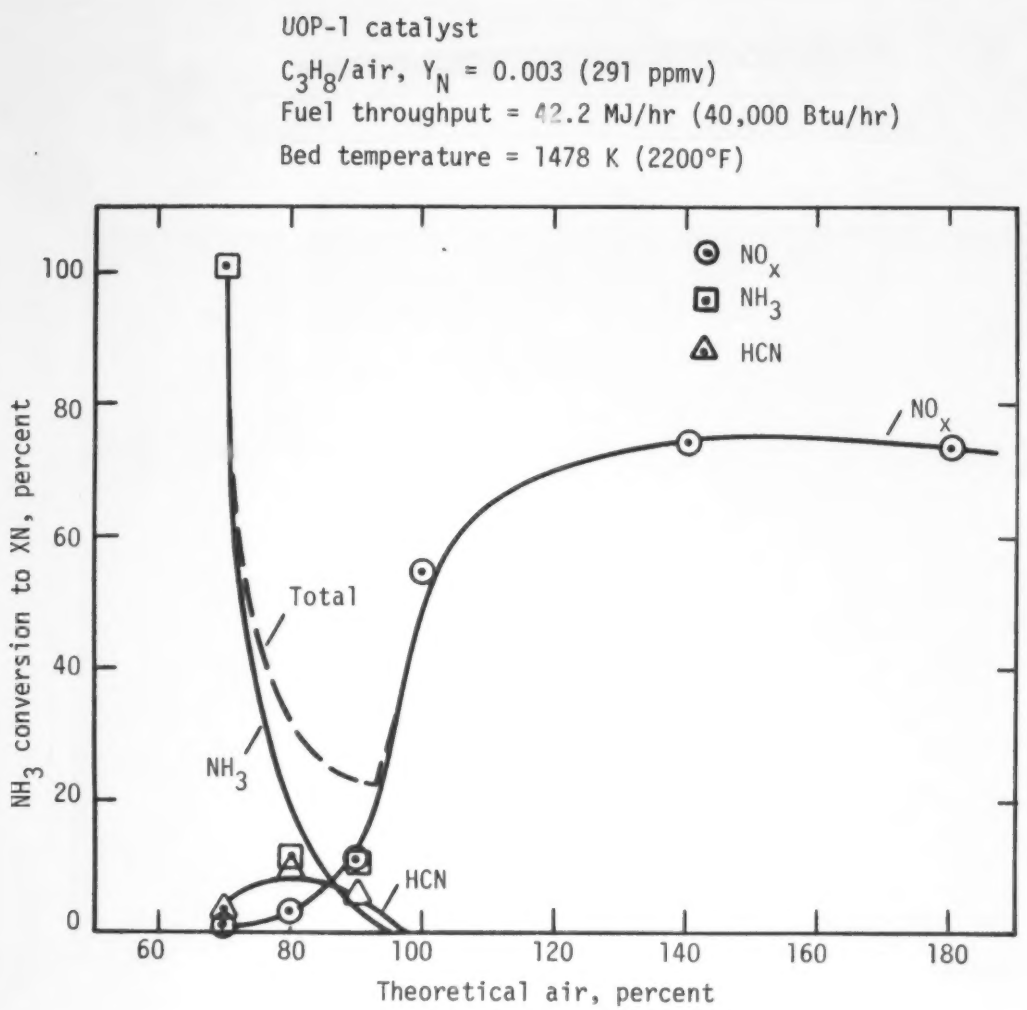


Figure B-6. NH_3 conversion at 1478 K, UOP-1 catalyst.

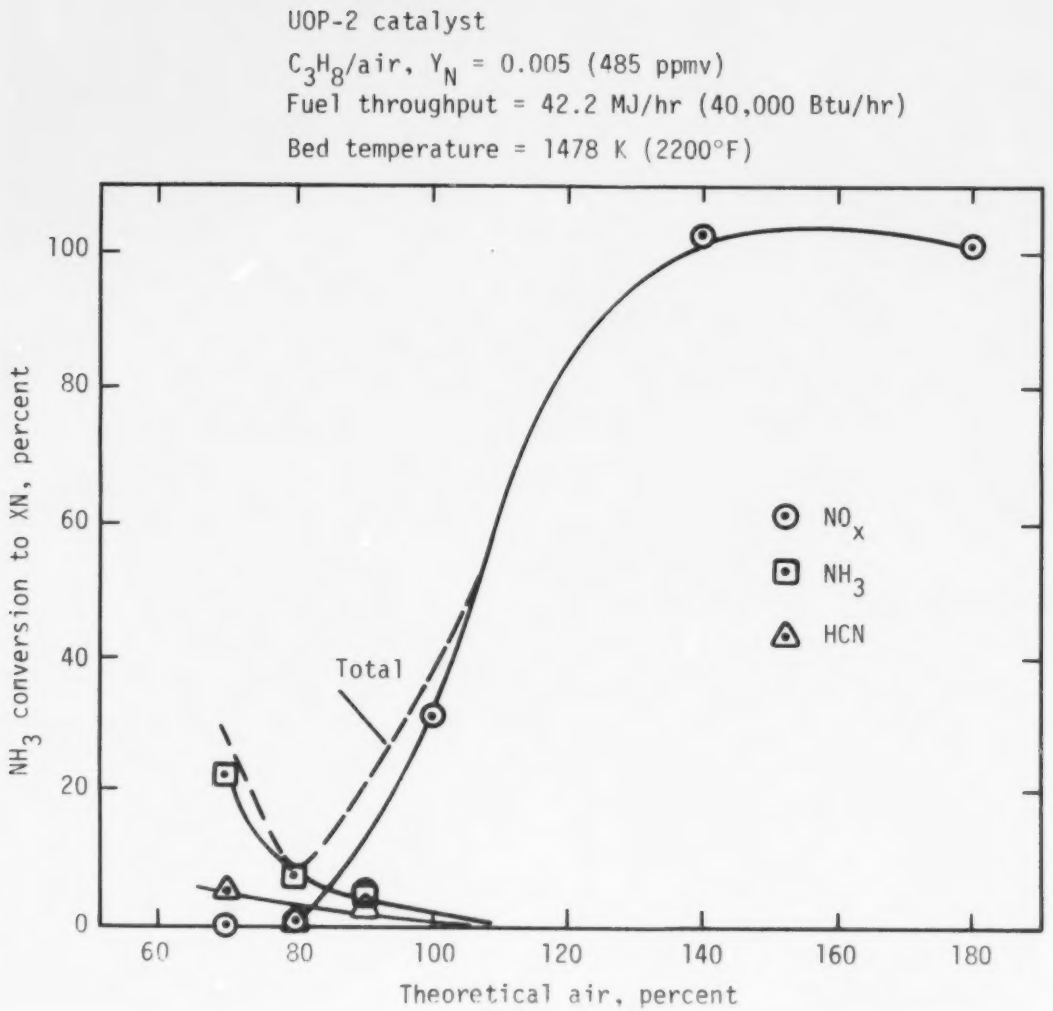


Figure B-7. NH_3 conversion at 1478 K, UOP-2 catalyst.

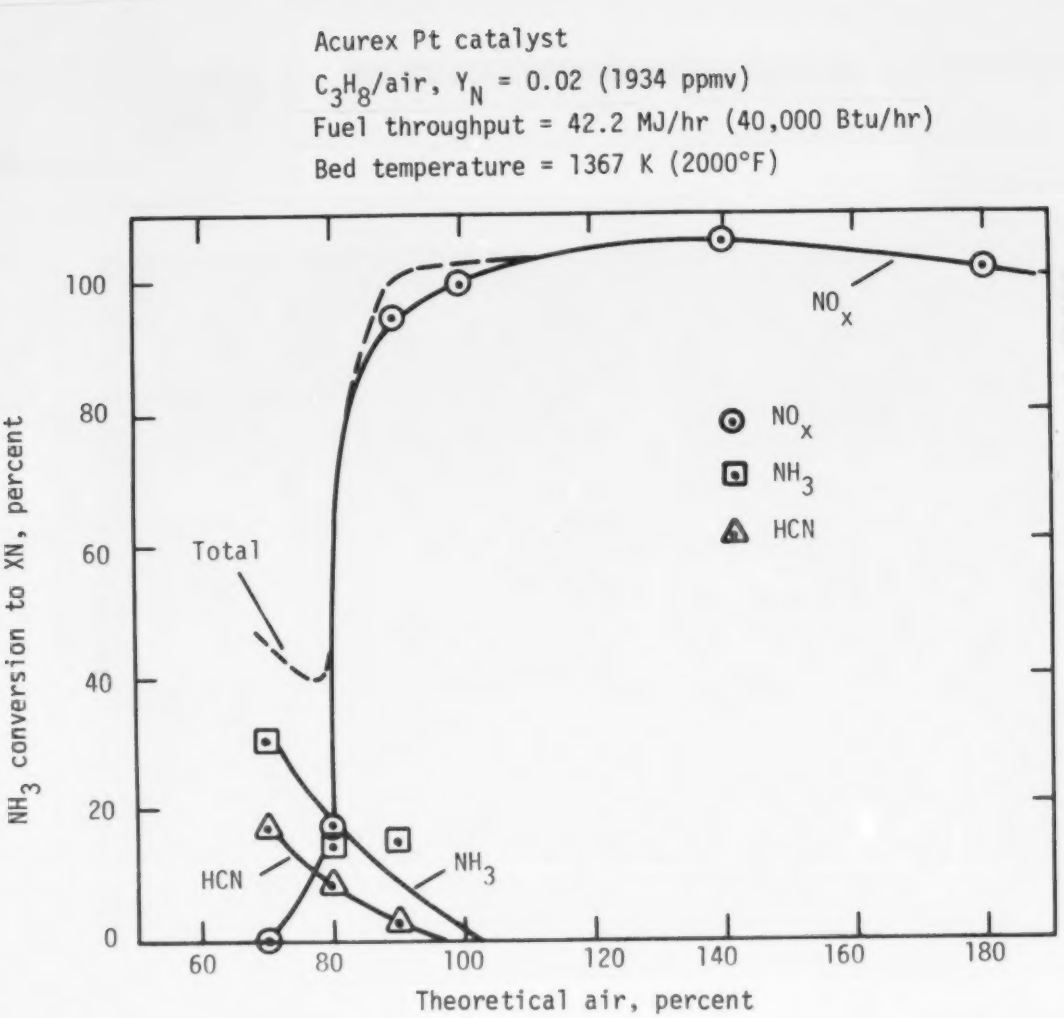


Figure B-8. NH_3 conversion at 1367 K, Acurex Pt catalyst.

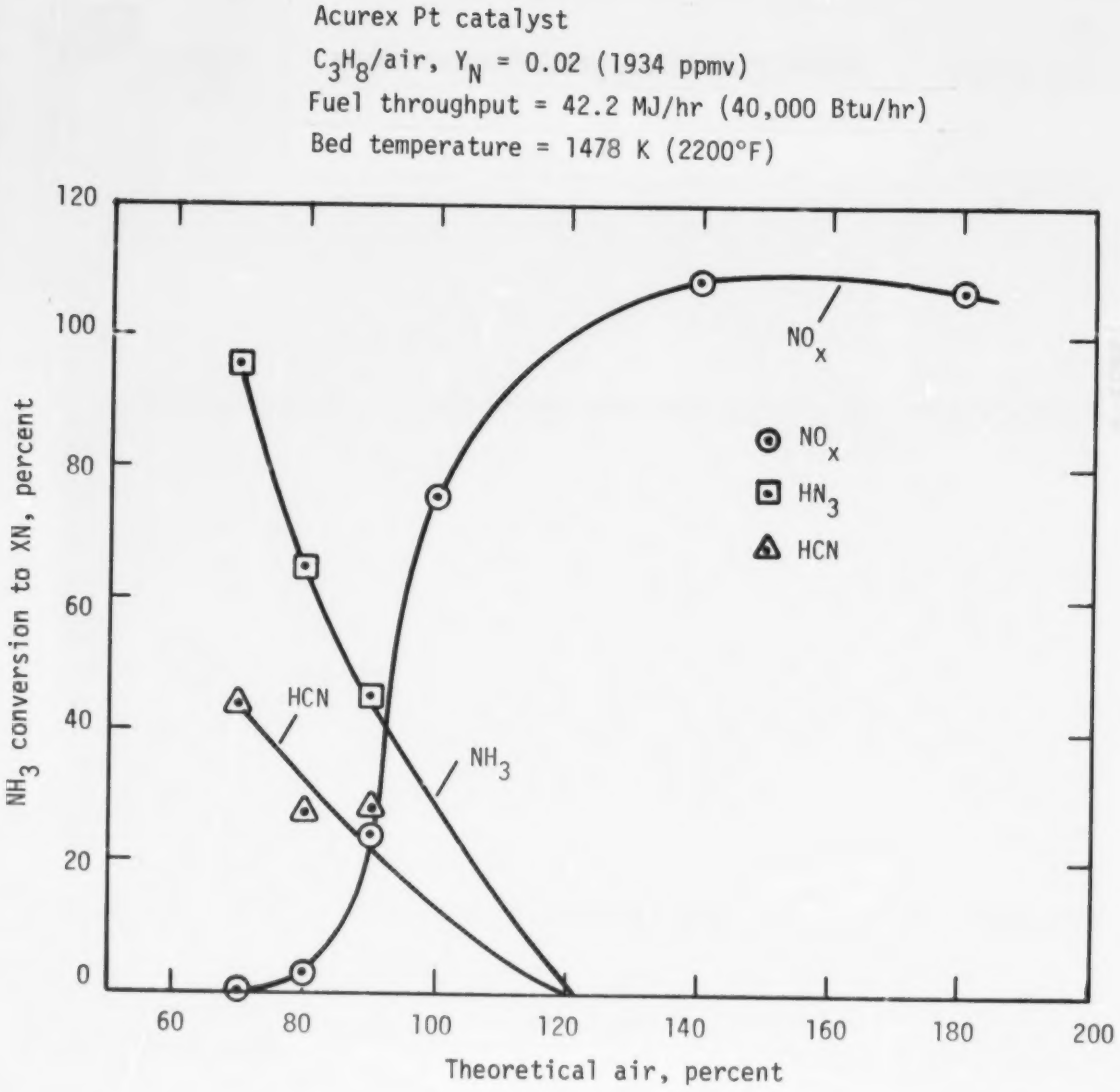


Figure B-9. NH_3 conversion at 1478 K, Acurex Pt catalyst.

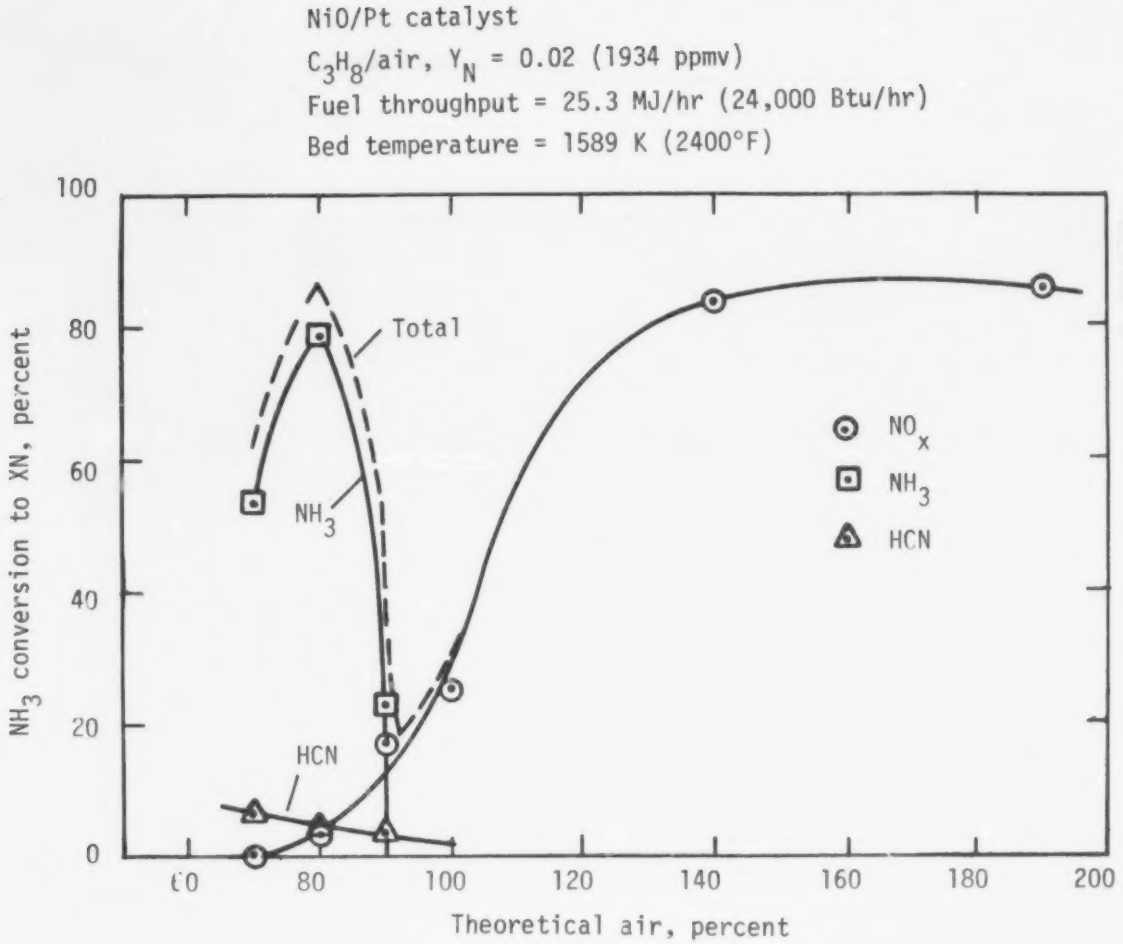


Figure B-10. NH_3 conversion at 1589 K, NiO/Pt catalyst.

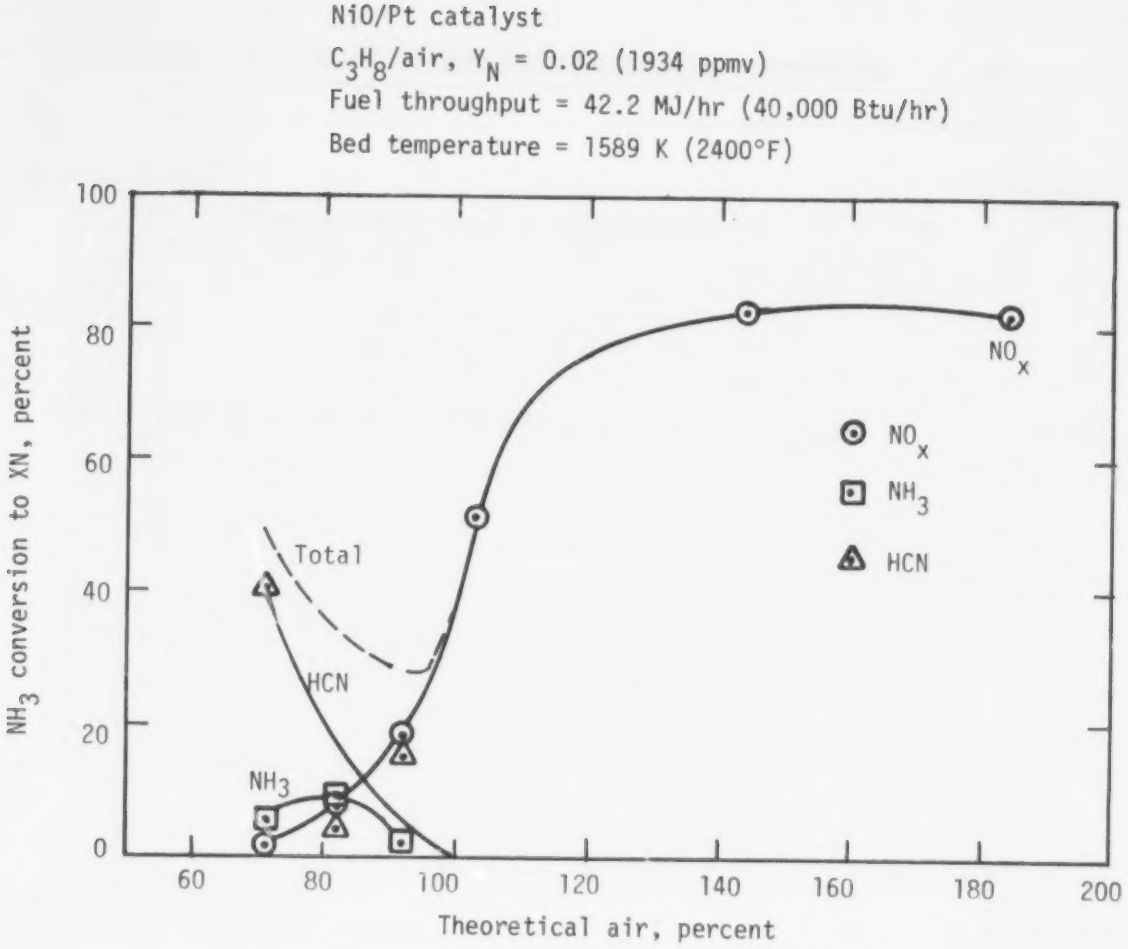


Figure B-11. NH_3 conversion at 1589 K, NiO/Pt catalyst.

APPENDIX C

N_2 CONCENTRATION MEASUREMENTS

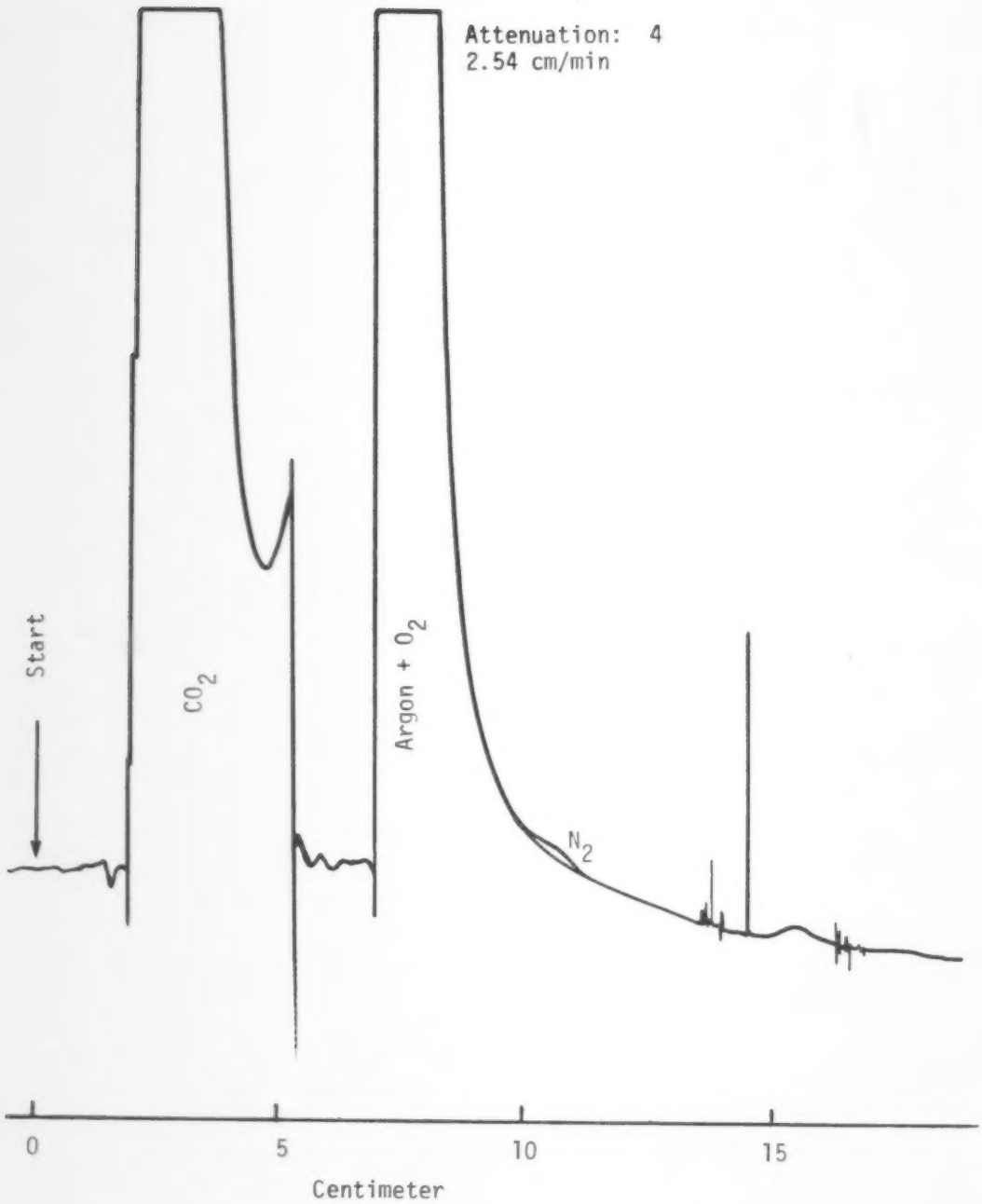


Figure C-1. Acurex Pt Catalyst, 97.5 percent TA, Y_N = 0.02.

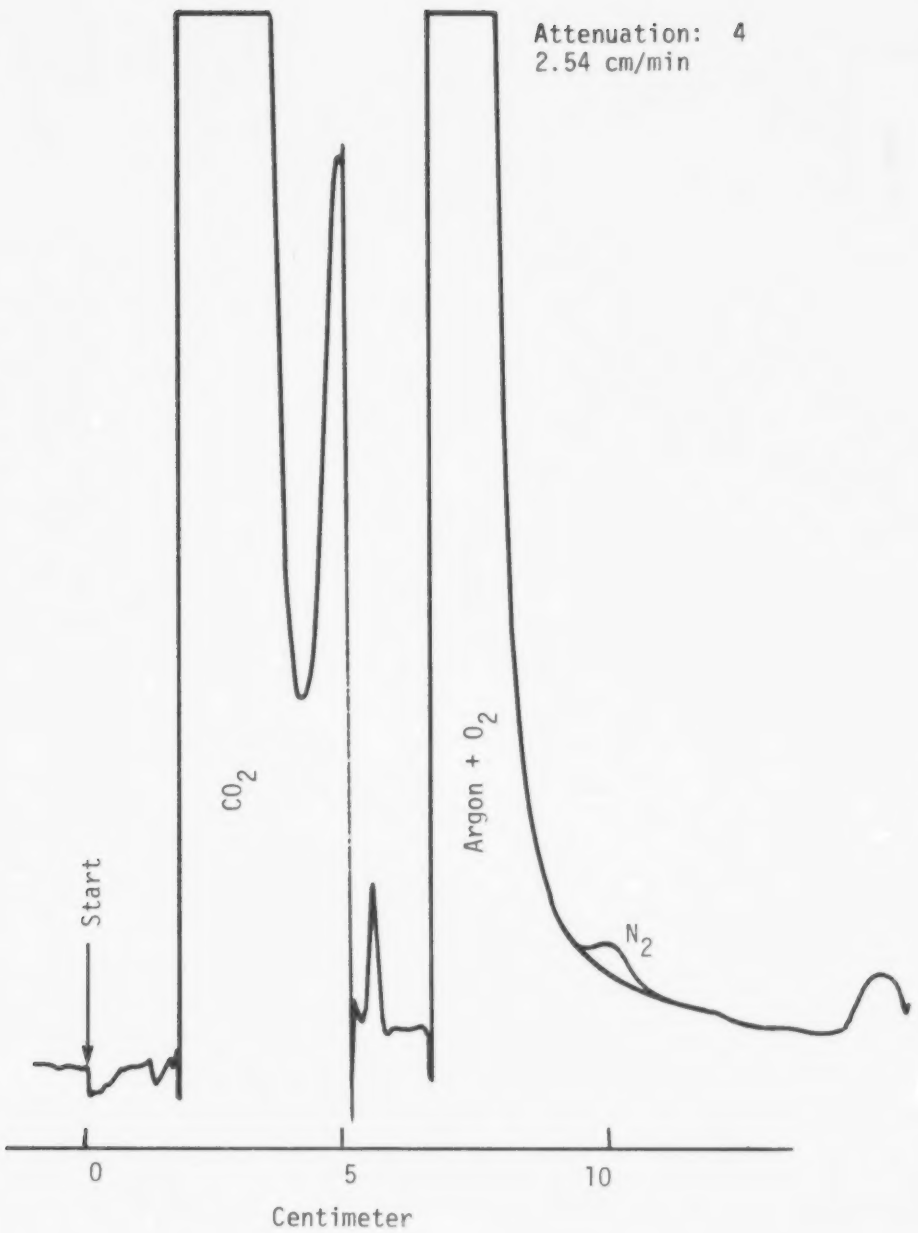


Figure C-2. Acurex Pt Catalyst, 75 percent TA, Y_N = 0.02.

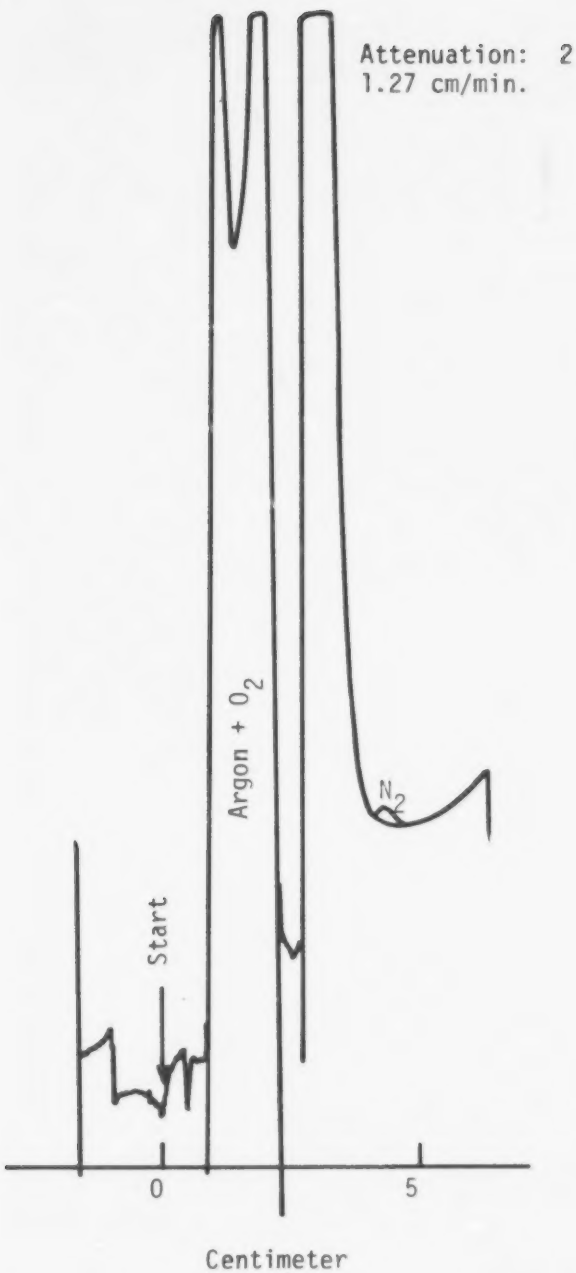


Figure C-3. Acurex NiO/Pt Catalyst, 20 percent TA, Y_N = 0.02.

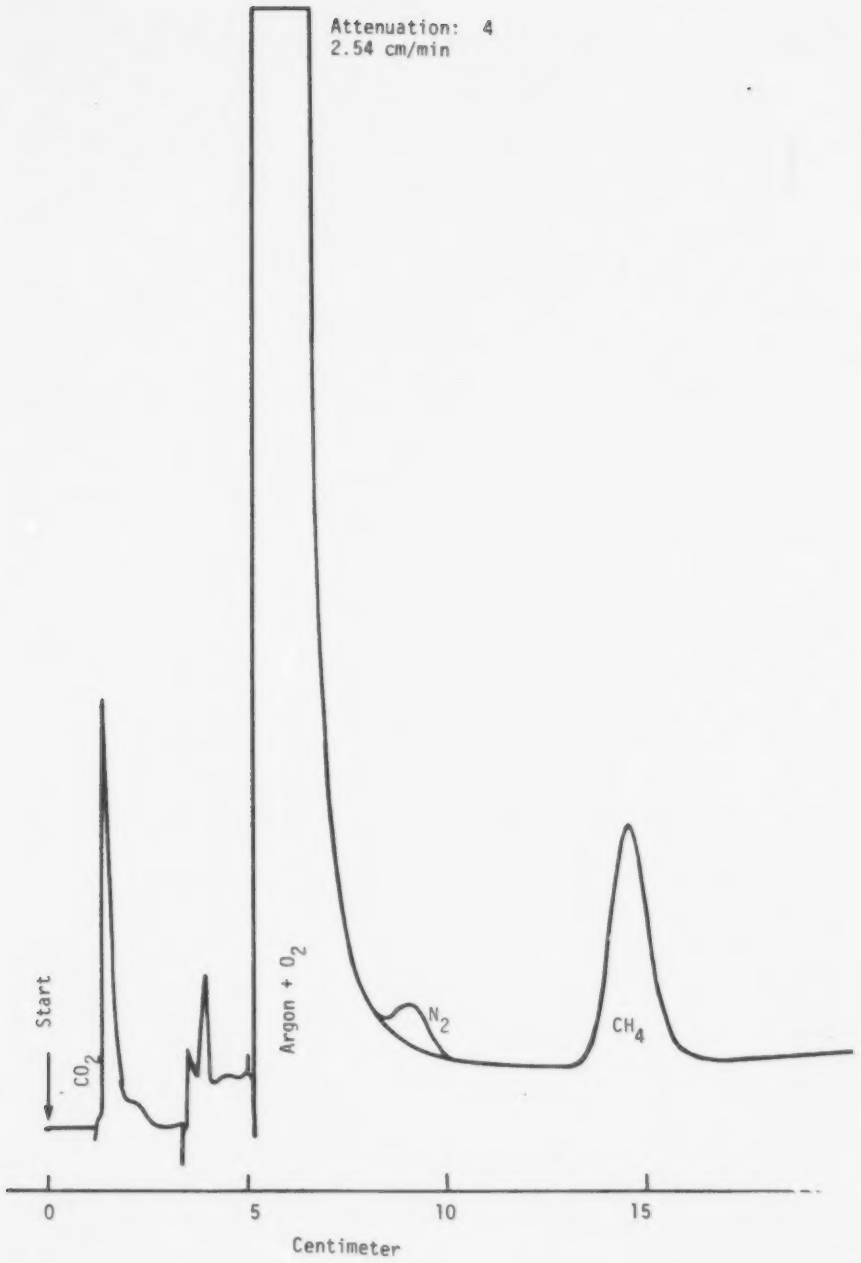


Figure C-4. Acurex NiO/Pt Catalyst, 75 percent TA, Y_N = 0.02.

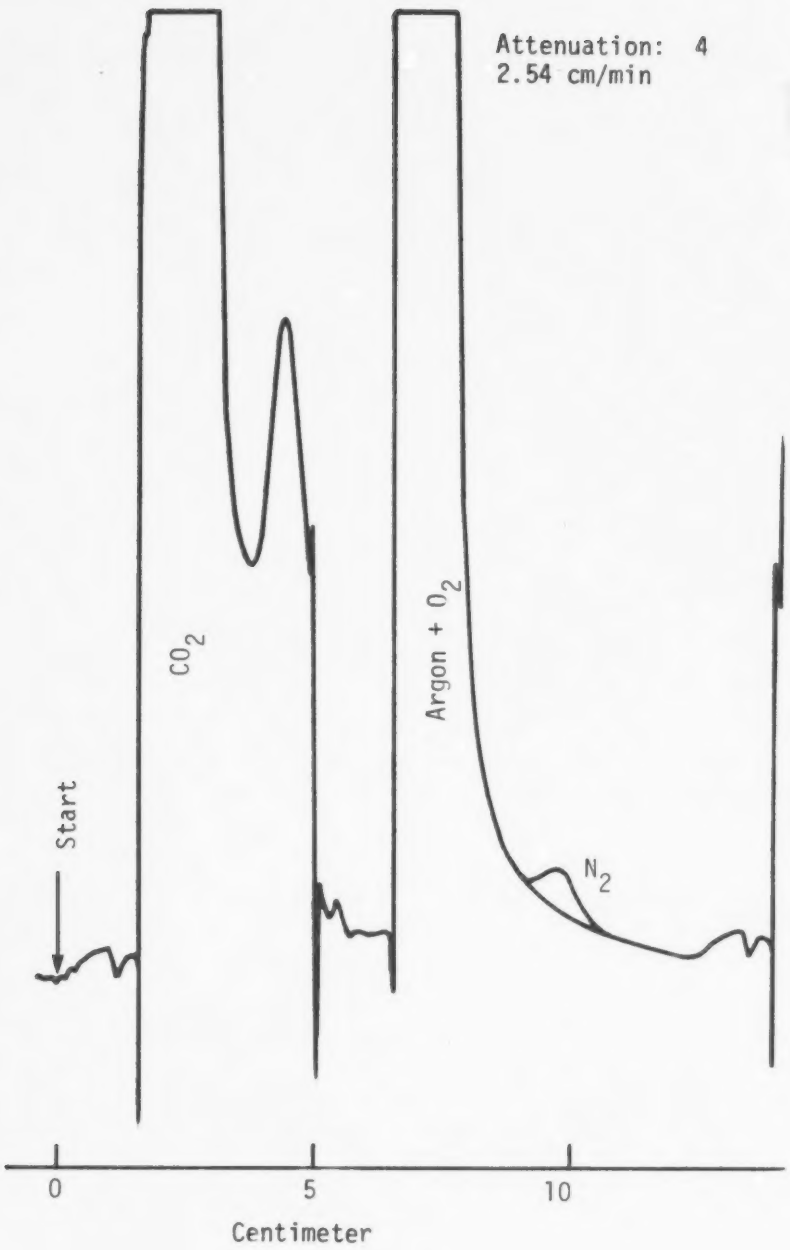


Figure C-5. UOP Catalyst, 100 percent TA, Y_N = 0.03.

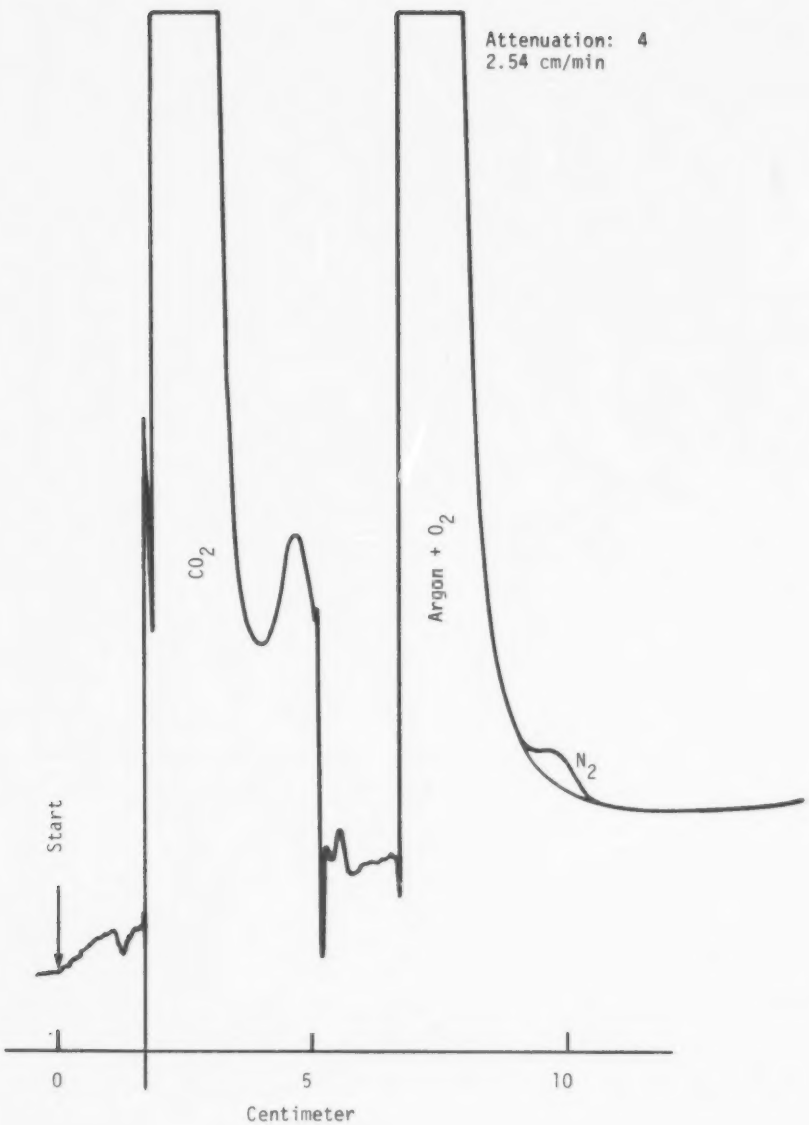


Figure C-6. UOP Catalyst, 90 percent TA, Y_N = 0.03.

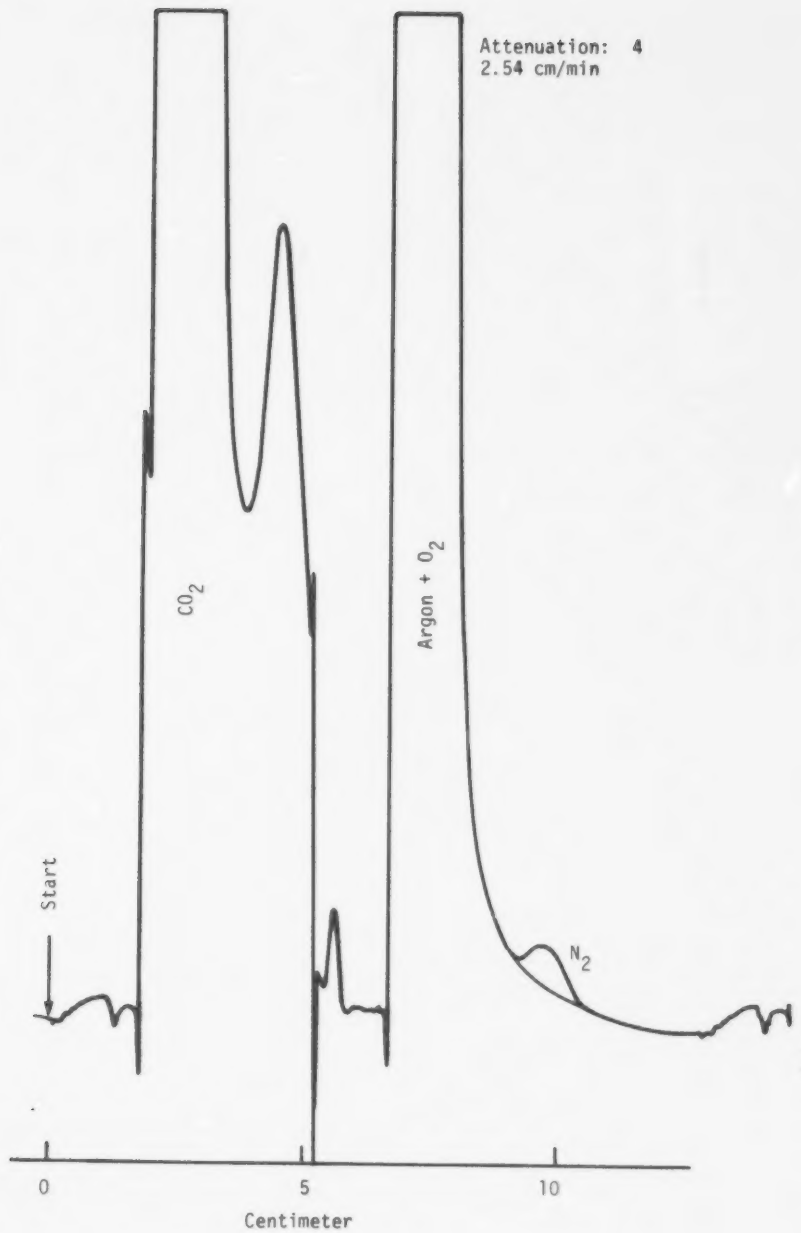


Figure C-7. UOP Catalyst, 80 percent TA, Y_N = 0.03.

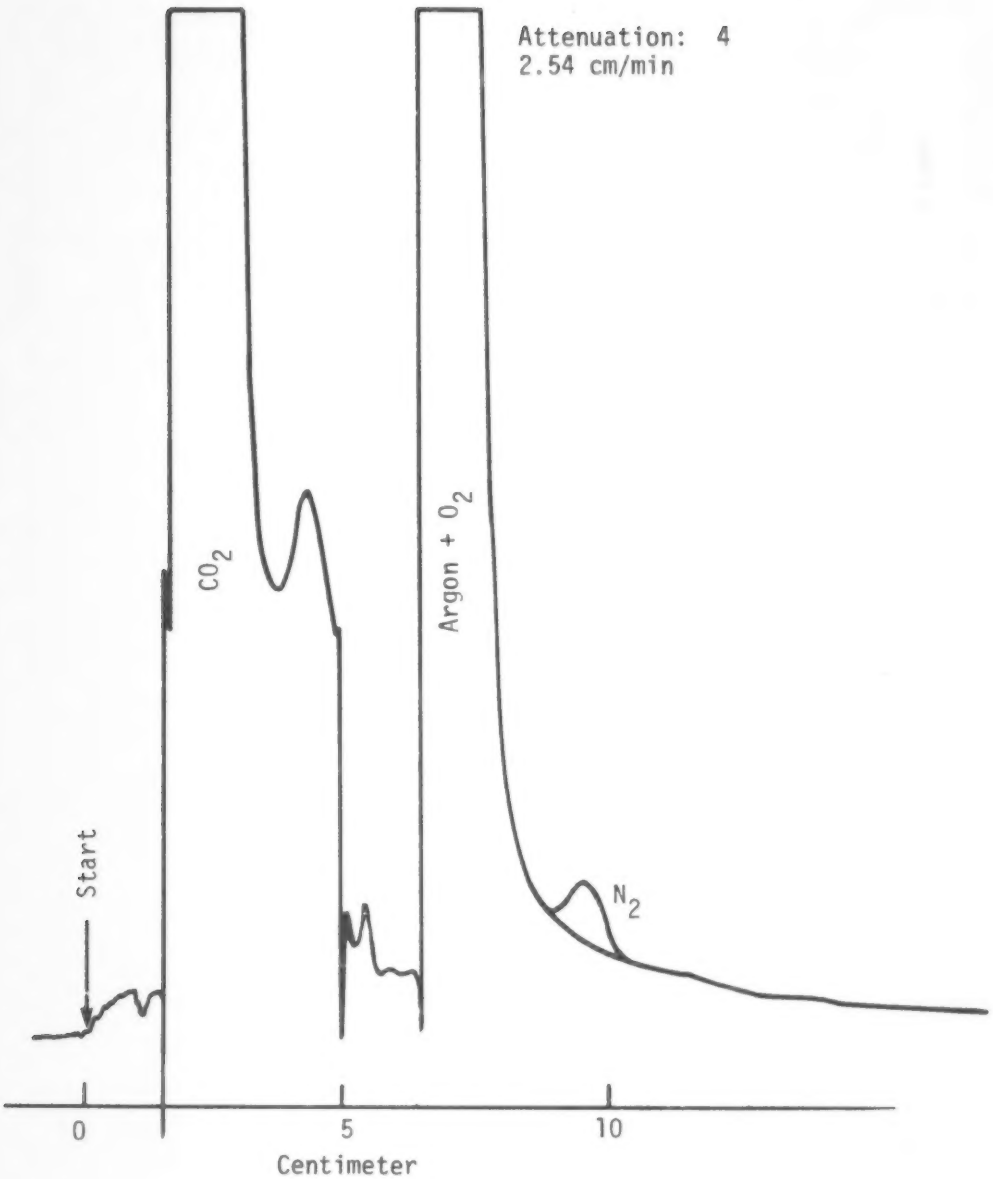


Figure C-8. UOP Catalyst, 75 percent TA, Y_N = 0.03.

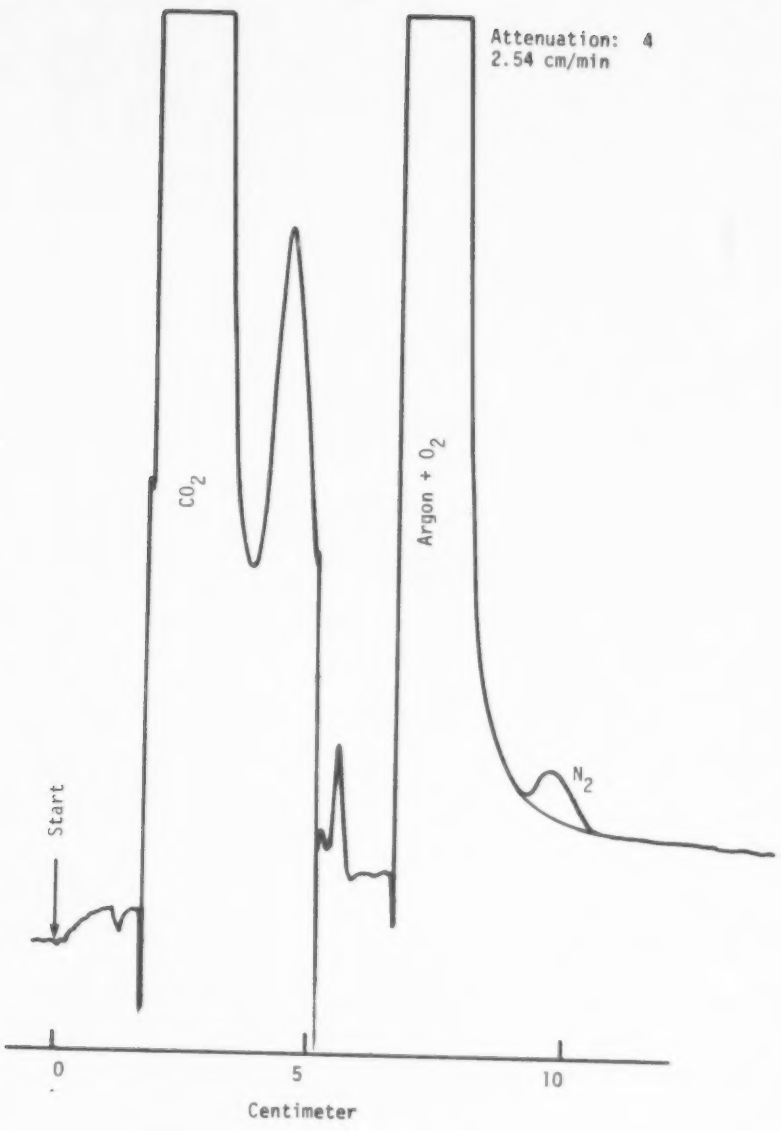


Figure C-9. UOP Catalyst, 70 percent TA, Y_N = 0.03.

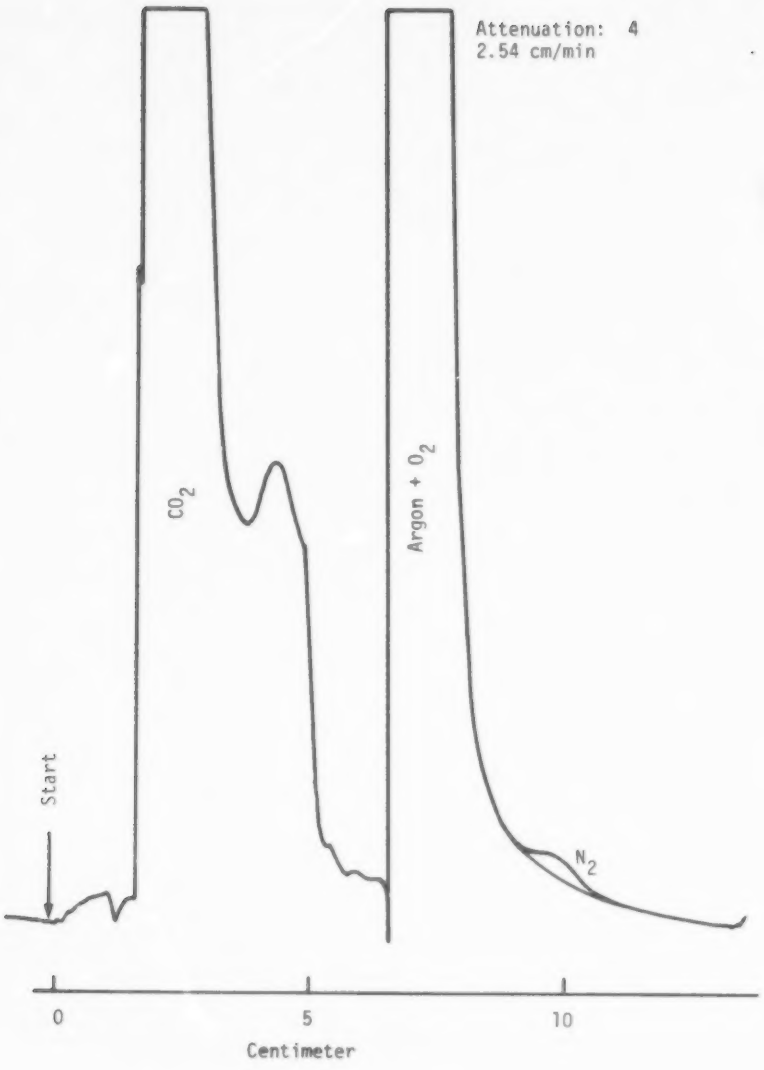


Figure C-10. UOP Catalyst, 100 percent TA, Y_N = 0.02.

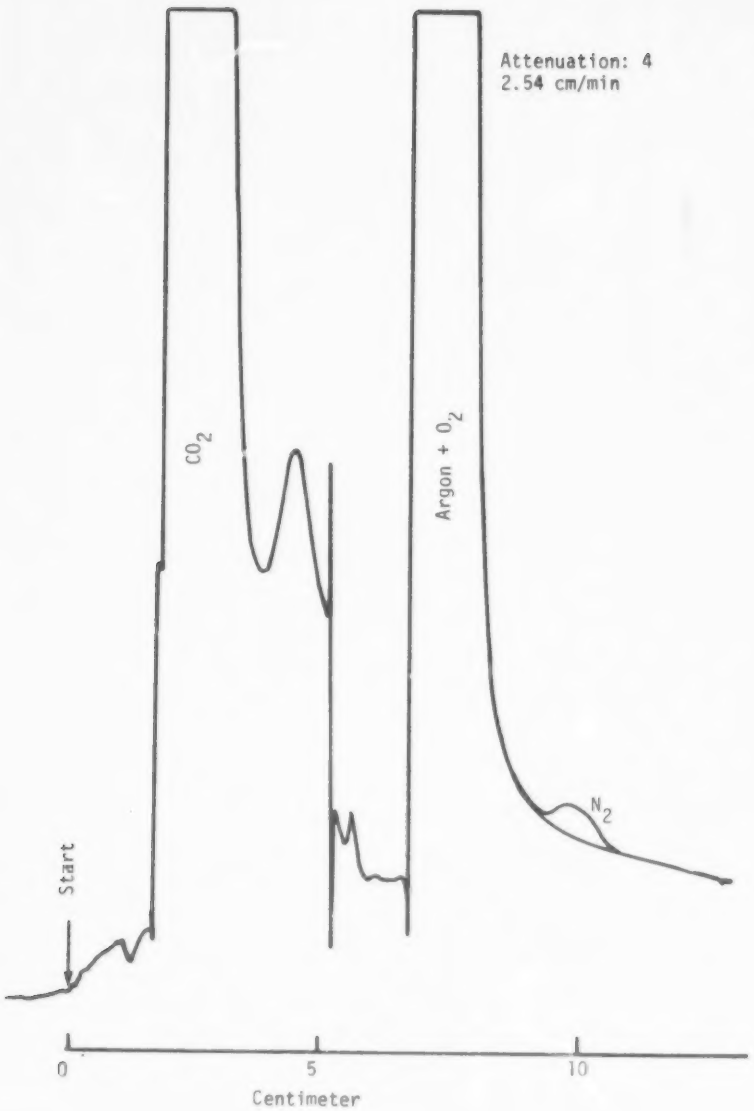


Figure C-11. UOP Catalyst, 75 percent TA, Y_N = 0.02.

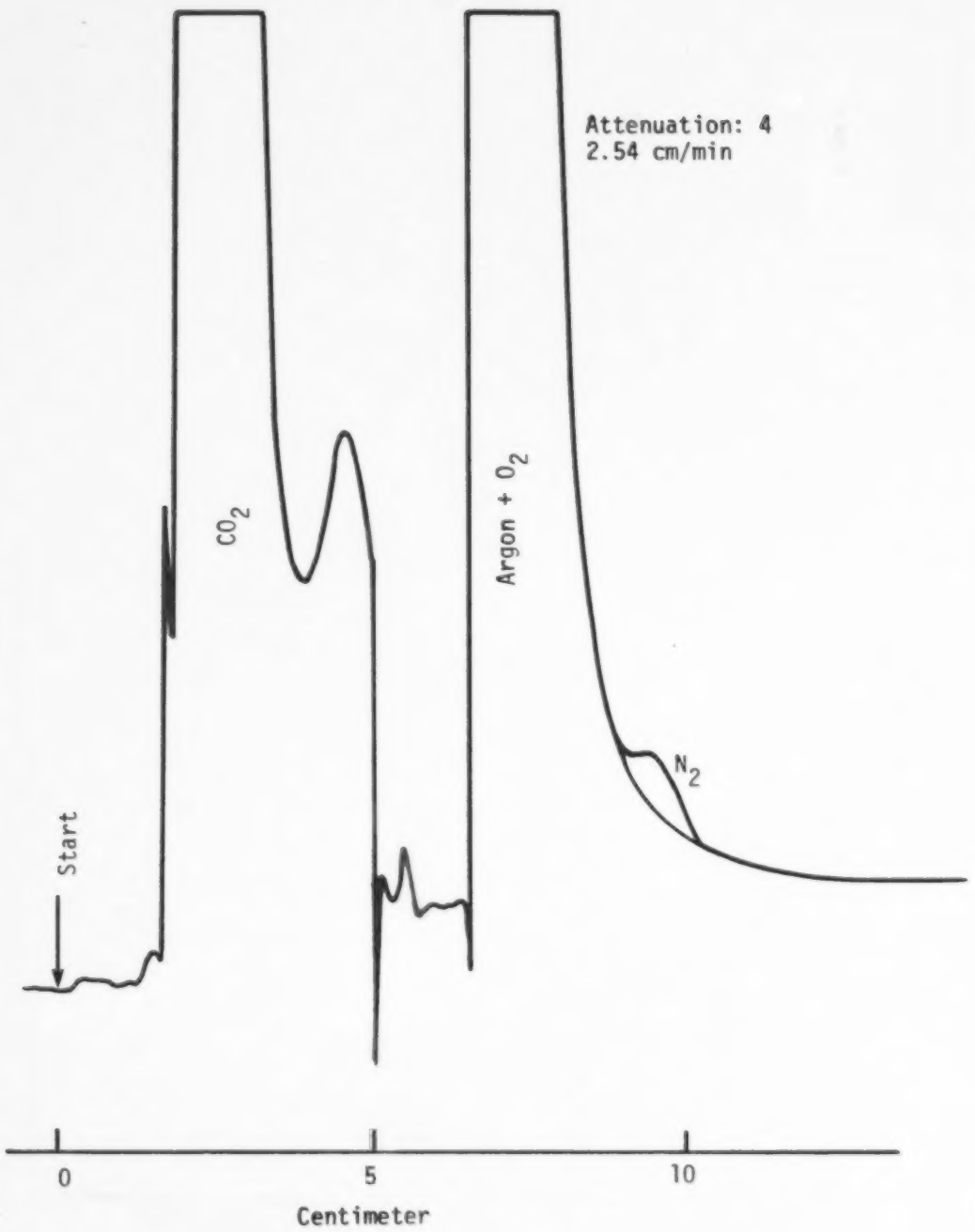


Figure C-12. UOP Catalyst, 90 percent TA, Y_N = 0.04.

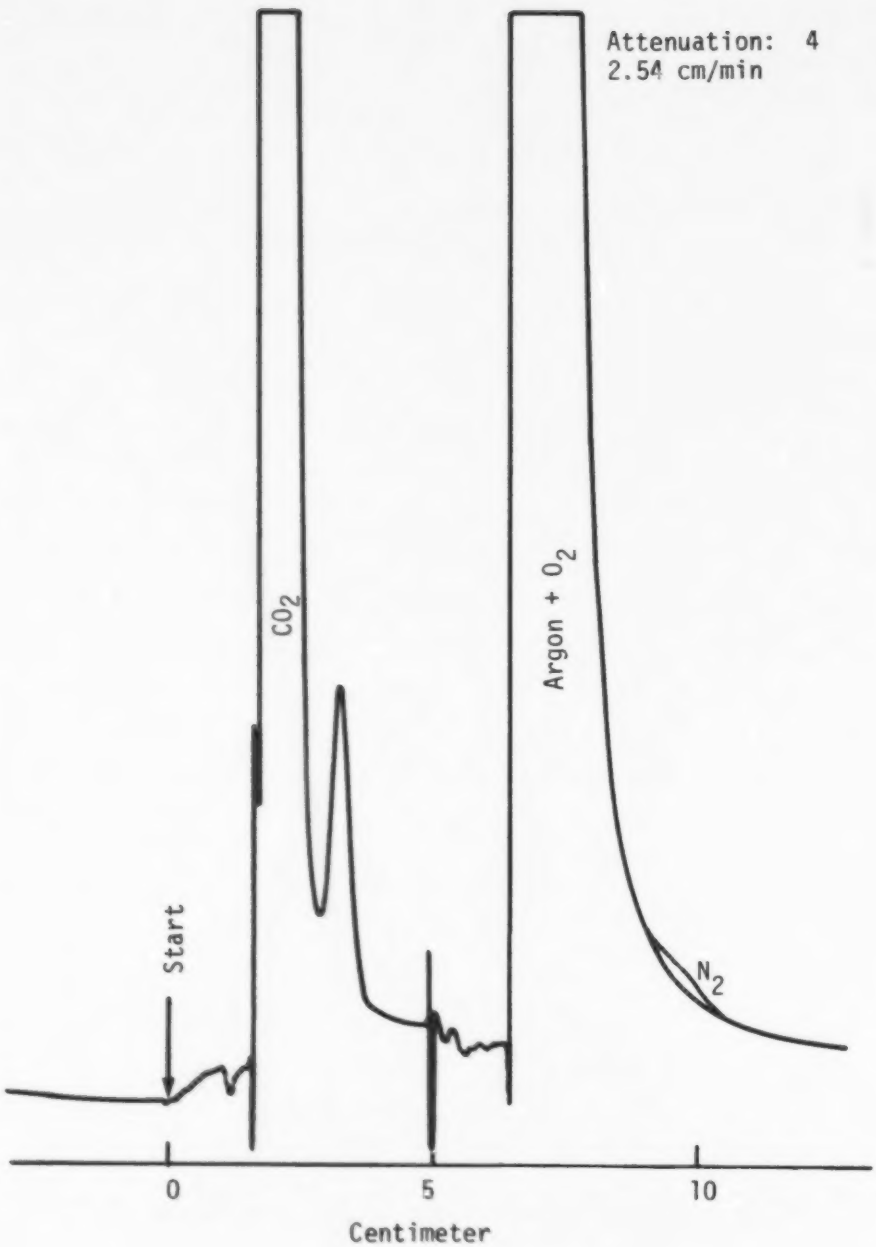


Figure C-13. UOP Catalyst, 100 percent TA, Y_N= 0.03, with H_2S.

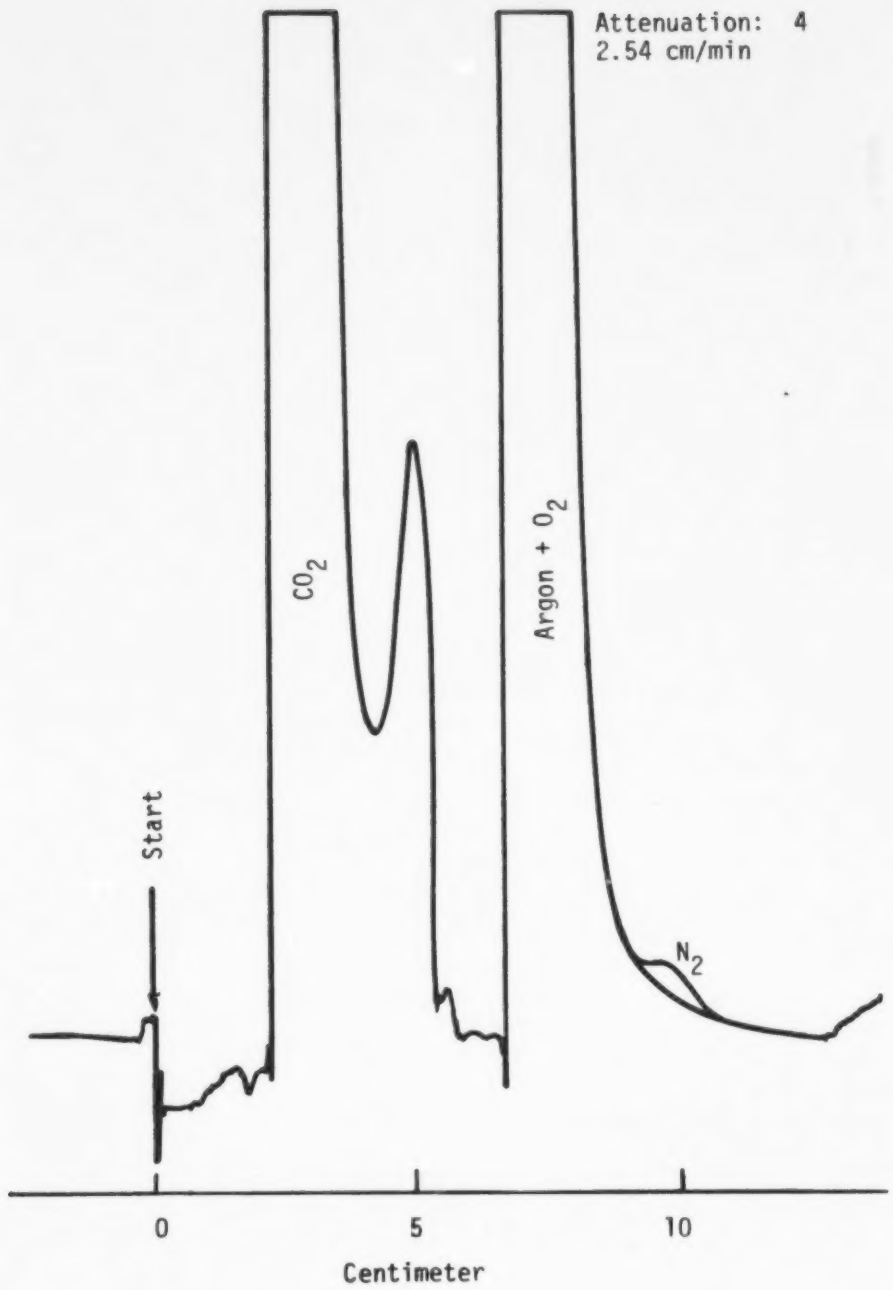


Figure C-14. UOP Catalyst, 90 percent TA, $Y_N = 0.04$, with H_2S.

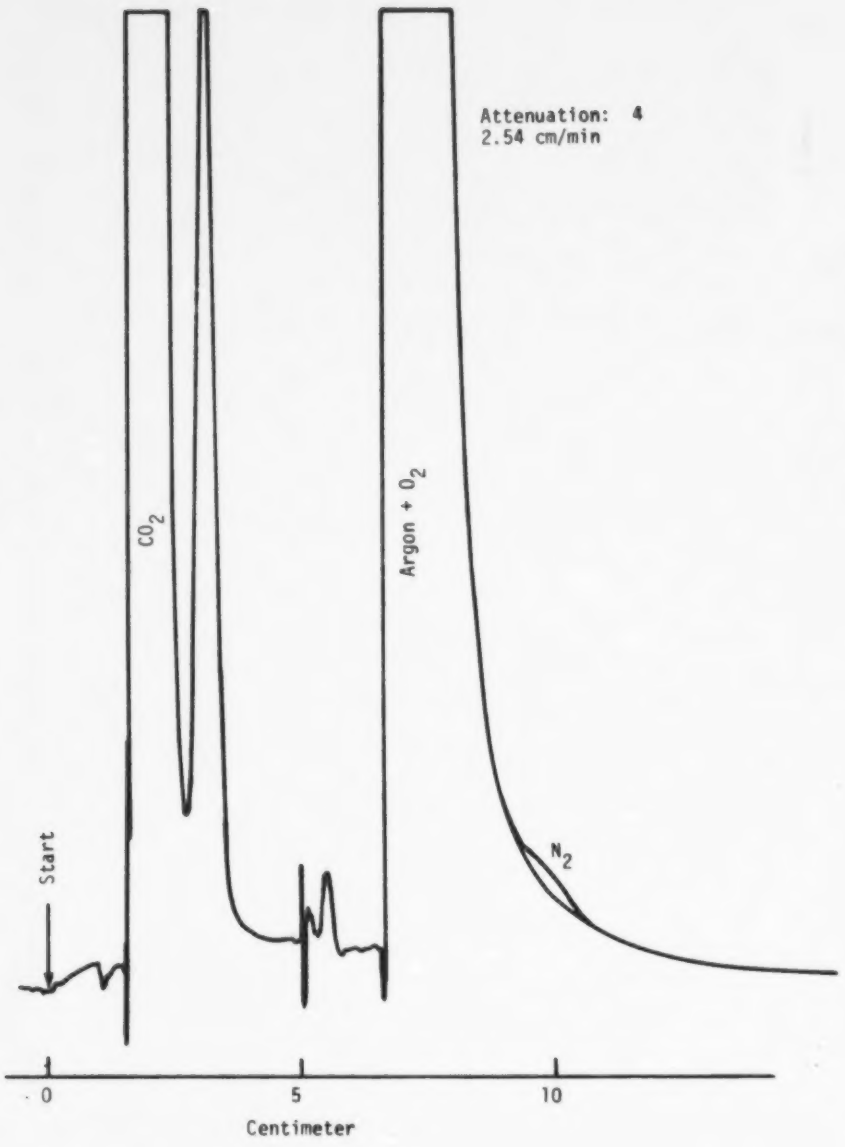


Figure C-15. UOP Catalyst, 80 percent TA, $Y_N = 0.03$, with H_2S.

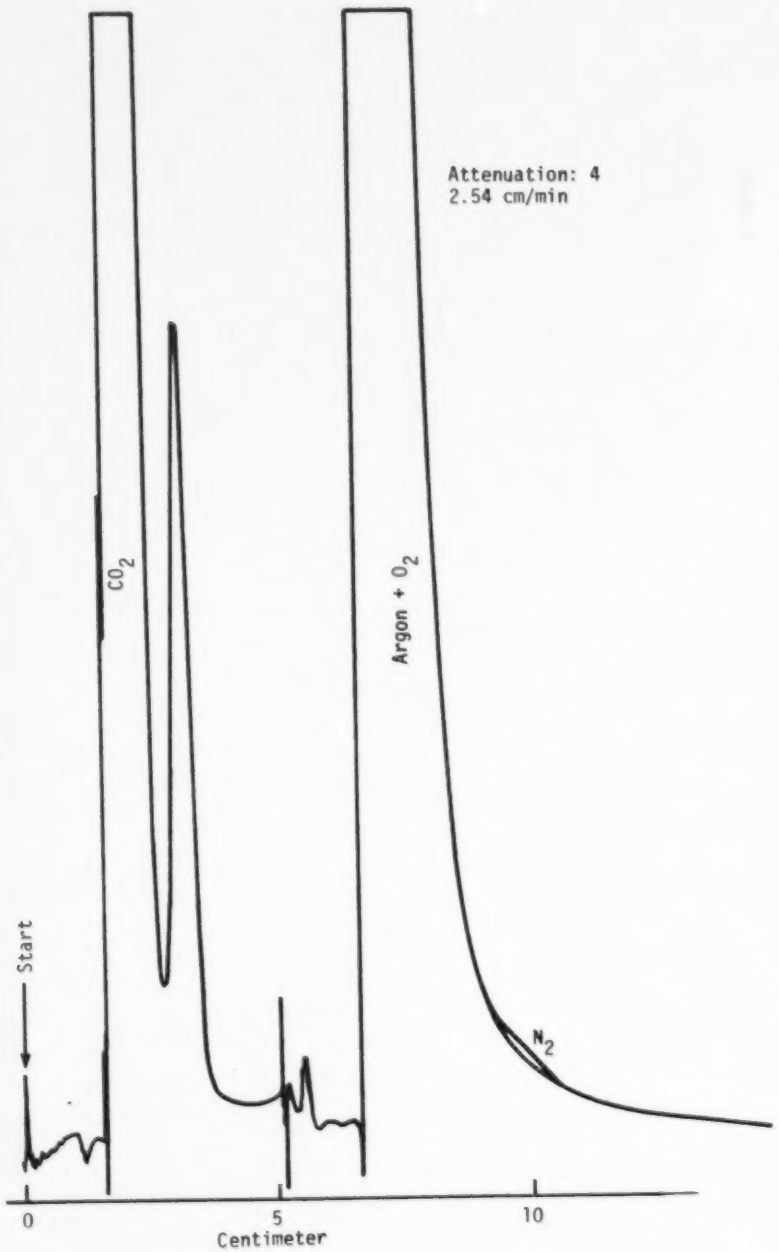


Figure C-16. UOP Catalyst, 75 percent TA, $Y_N = 0.03$, with H_2S.

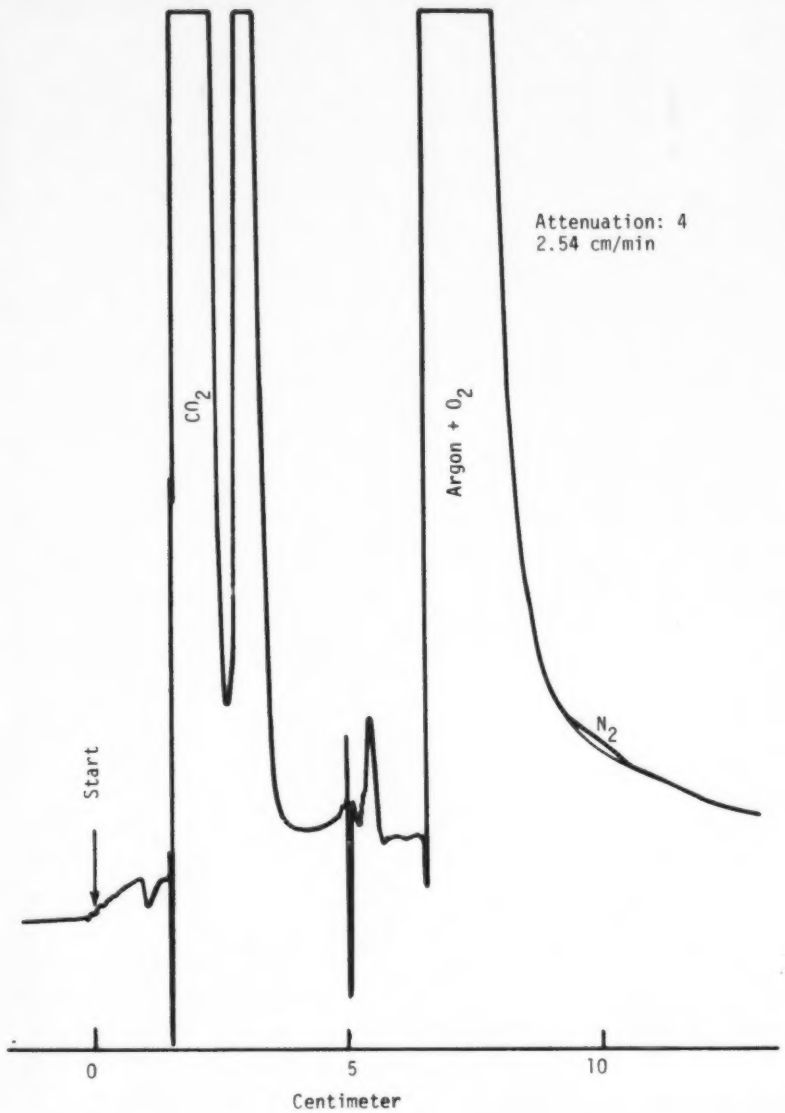


Figure C-17. UOP Catalyst, 70 percent TA, $Y_N = 0.03$, with H_2S.

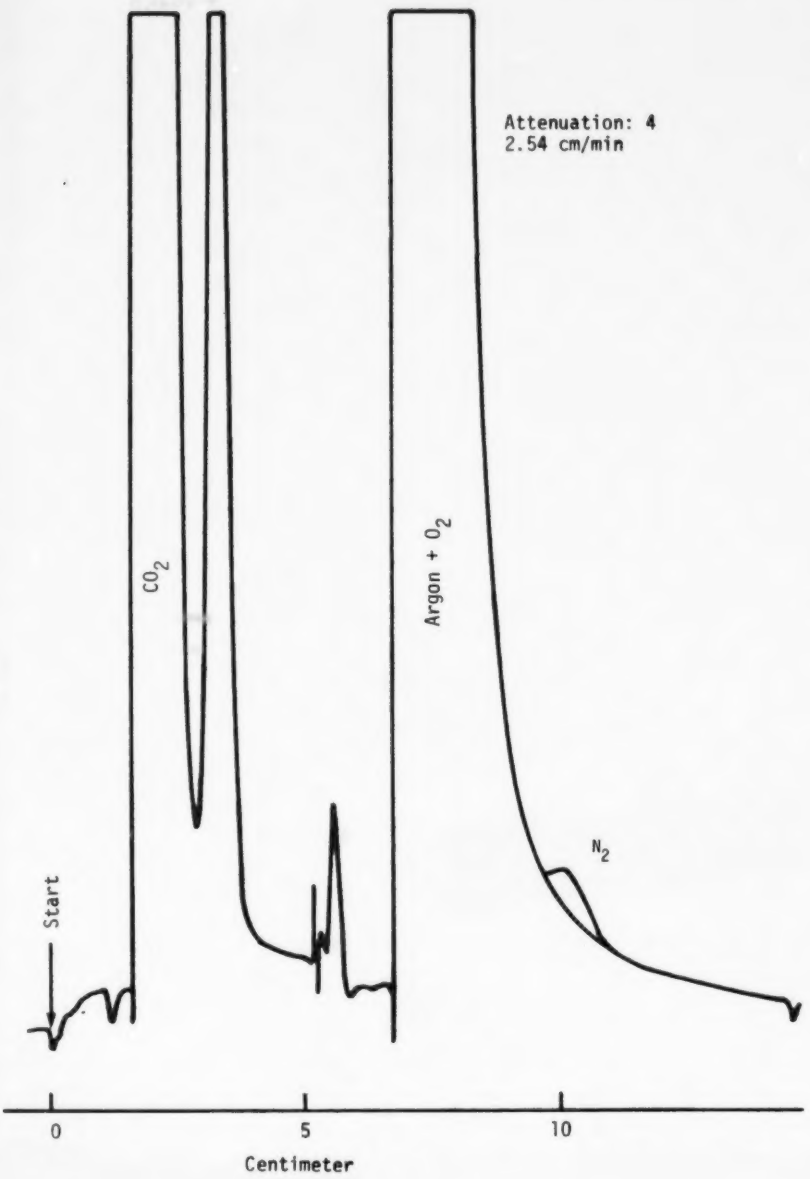


Figure C-18. Aged UOP Catalyst, 80 percent TA, Y_N = 0.03.

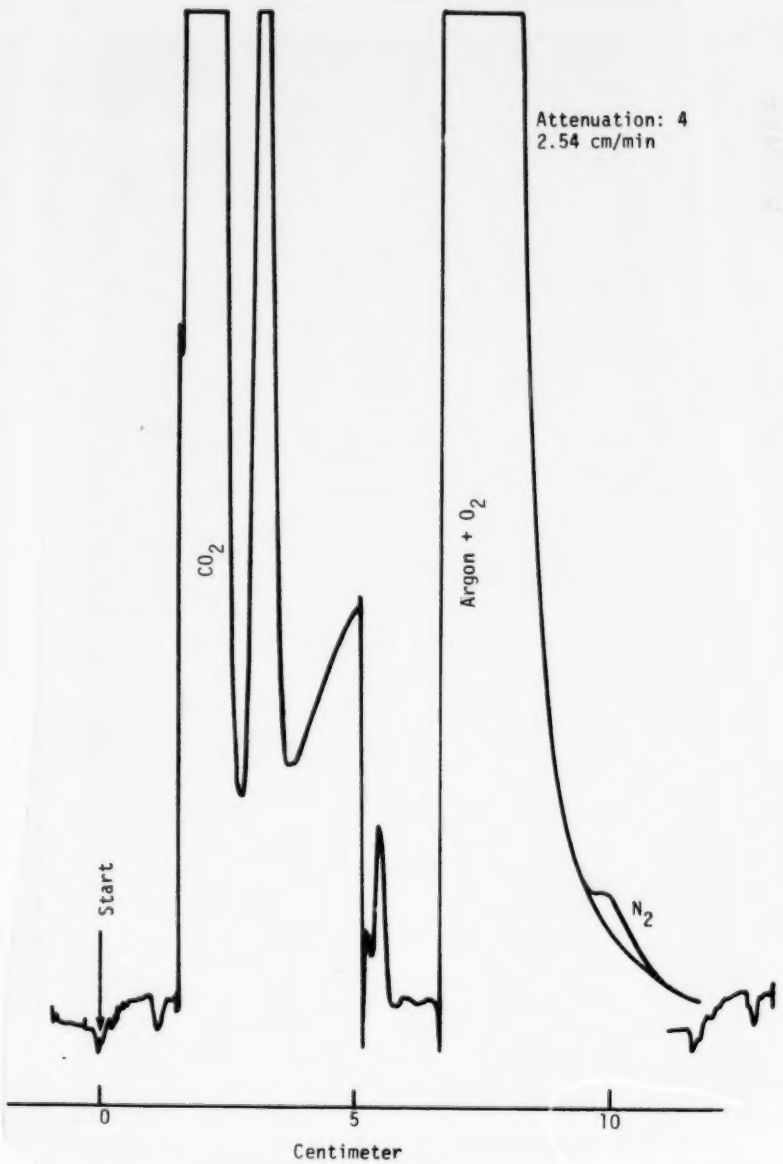


Figure C-19. Aged UOP Catalyst, 70 percent TA, Y_N = 0.03.